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THREE-PARTICLE COLLISION INTEGRALS FOR THERMAL CONDUCTIVITY, VISCOSITY AND SELF-DIFFUSION OF A GAS OF HARD SPHERICAL MOLECULES. PART I. THEORY

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FOREWORD

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ABSTRACT

The transport porperties of a dilute gas are determined by binary collision integrals. In order to predict the first density corrections to the transport properties, it is necessary to consider collision integrals that account for the effects of collisions among three molecules. In this technical report we derive and formulate such three-particle collision integrals for the coefficients of thermal conductivity, viscosity and self-diffusion of a gas of hard spherical molecules. An evaluation of these three-particle collision integrals will be presented in a subsequent technical report.

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I. Introduction

The theory for the transport properties of dilute gases consisting of spherically symmetric molecules is well established. This theory is based on the Boltzmann equation, which can be solved using a procedure introduced by Chapman and Enskog. The transport properties are thereby expressed in terms of binary collision integrals. Calculation of these binary collision integrals has become a routine procedure, and tabulated values are available for many forms of the intermolecular potential [1,2].

The validity of the Boltzmann equation is restricted to the low density limit. In order to evaluate the transport properties of a moderately dense gas we consider an expansion in terms of the density. Originally, it was envisaged that the transport properties could be represented by a *power* series in the density, in obvious analogy to the virial expansion for the compressibility factor. Subsequent developments, to some extent discussed in AEDC-TR-69-68 [3], have revealed that the density dependence of the transport properties is more complicated, and that terms logarithmic in the density appear also.† That is, the density expansions for the thermal conductivity λ, the shear viscosity η and self-diffusion coefficient D are of the form

† For a bibliography on the subject see Ref. [4].

$$\lambda = \lambda_o+\lambda_1 n+\lambda_2 n^2 \log n+\cdots$$

$$\eta = \eta_o+\eta_1 n+\eta_2 n^2 \log n+\cdots \qquad (1.1)$$

$$nD = D_o+D_1 n+D_2 n^2 \log n+\cdots$$

where n is the number density. The lowest order terms λ_o, η_o and D_o are given by the Chapman-Enskog theory. In this report we focus our attention on the coefficients λ_1, η_1 and D_1 of the contributions linear in the density. Empirical values for the coefficients λ_1 and η_1 of a number of gases were reported in AEDC-TR-69-68 and AEDC-TR-71-190 [3,5,6]. In order to calculate these coefficients from the theory, it is necessary to evaluate collision integrals that are related to sequences of collisions among *three* molecules [3].

Prior to the systematic developments, Enskog made an intuitive attempt to generalize the Boltzmann equation to a dense gas of hard spheres [7]. The Boltzmann equation is akin to the perfect gas law in that it neglects any correlations in the positions of the molecules; furthermore, the velocities of two molecules which are about to collide are also assumed to be uncorrelated (assumption of molecular chaos). In the theory of Enskog for dense gases an estimate was made to account for the effect of correlations in configuration space; they were assumed to be the same as those for a gas in equilibrium. The assumption of molecular chaos was retained for the probability distribution in

velocity space.

In a previous report estimates for the complete triple collision integrals were presented for a gas of hard spherical molecules [3,8]. It turned out that their contribution differed by less than ten percent from the value predicted by the theory of Enskog. This conclusion was recently confirmed by Henline and Condiff [9].

In this report we shall show that for a gas of hard spheres the theory of Enskog is recovered as the first approximation, when the collision integrals are expanded in terms of the number of successive binary collisions between the molecules. For this purpose it is important to make a distinction between the effects of *statistical* versus *dynamical* correlations. In the equilibrium case the first density correction to the radial distribution function of particles 1 and 2 is determined by those configurations for which a third particle is overlapping with both particles 1 and 2. That is, the configurations which determine the excluded volume are those for which the center of the third particle would lie inside the action spheres of both particles 1 and 2. If in the *non-equilibrium case* the integration in the triple collision integral is restricted to the same configurations, the triple collision integral yields for the first density correction the equilibrium radial distribution function multiplied with the Boltzmann collision

integral [3]. This is precisely the contribution given by the Enskog theory and it contains, effectively, the dynamics of only one binary collision among the three particles. Deviations from molecular chaos can then be incorporated in successive higher approximations by considering correlations brought about by two, three and four successive collisions among the particles. The details of this expansion will become more clear in Sections IV and V.

The purposes of this report are:

a) to present a simple, self-contained derivation of the three-particle collision integrals that bypasses the somewhat intricate surface integration method proposed by Green [10] and further developed in previous technical reports [3,11].

b) to elucidate how an analysis of the statistical and dynamical correlations, caused by the interactions of three molecules, leads to a decomposition of the collision integrals associated with the number of successive collisions among three particles.

c) to express the three-particle collision integrals in a form suitable for a quantitative evaluation of these integrals.

The treatment is restricted to a gas of hard spherical molecules. In this case the molecular dynamics reduces to sequences of successive binary collisions among the molecules.

The analysis is simplified by the fact that we do not need to consider more than four collisions as demonstrated by Hoegy and Sengers [12] and reported in AEDC-TR-71-51 [11].

We shall proceed as follows. Non-equilibrium statistical mechanics relates the transport properties to time correlation functions of the corresponding fluxes [13]. Starting from these time correlation functions we show in Section II how the first density corrections to the transport properties are determined by matrix elements involving a triple collision operator. This triple collision operator can be represented by a binary collision expansion. The properties of the binary collision operators are summarized in Section III. In that section we also develop a diagrammatic notation to elucidate the meaning of the various terms in the binary collision expansion. In Section IV we use the binary collision expansion to decompose the triple collision operator into a series of terms accounting for increasingly higher order dynamical correlations. In Section V we specify the corresponding three-particle collision integrals. The first density corrections λ_1, η_1, D_1 to the transport coefficients are thus determined by a set of collision integrals involving the dynamics of one, two, three and four successive collisions among three molecules. The results are discussed in Section VI.

II. Transport coefficients in terms of collision operators.

The transport coefficients for a system of particles at temperature T and number density n can be expressed as integrals of time correlation functions of the corresponding fluxes [13]

$$\lambda = \frac{1}{3kT^2} \lim_{\varepsilon\to 0} \lim_{V\to\infty} \int_0^\infty dt\ e^{-\varepsilon t} V^{-1} \langle \vec{J}_\lambda \cdot \vec{J}_\lambda(t) \rangle \quad ,$$

$$\eta = \frac{1}{10kT} \lim_{\varepsilon\to 0} \lim_{V\to\infty} \int_0^\infty dt\ e^{-\varepsilon t} V^{-1} \langle \vec{\vec{J}}_\eta : \vec{\vec{J}}_\eta(t) \rangle \quad , \tag{2.1}$$

$$nD = \frac{1}{3} \lim_{\varepsilon\to 0} \lim_{V\to\infty} \int_0^\infty dt\ e^{-\varepsilon t} V^{-1} \Big\langle \sum_{i=1}^{N} \vec{v}_i \cdot \vec{v}_i(t) \Big\rangle \quad ,$$

where k is Boltzmann's constant and $n = \langle N \rangle / V$. The average $\langle\ \rangle$ is taken over an equilibrium ensemble, for which we choose a grand canonical ensemble with temperature $T = (k\beta)^{-1}$ and chemical potential μ. Thus for any phase function $X(x_1, x_2 \ldots x_N) = X(12\ldots N)$

$$\langle X \rangle = \sum_N \frac{z^N}{N! Z} \int dx^N \prod_{i=1}^{N} \phi(v_1) W(12\ldots N) X(12\ldots N). \tag{2.2}$$

The grand partition function Z is defined such that $\langle 1 \rangle = 1$; the activity $z = (2\pi m/\beta h^2)^{3/2} \exp(\beta\mu)$, where h is Planck's constant and m the mass of a particle; $dx^N = dx_1 \ldots dx_N$ is a volume element in phase space and the phase $x_i = (\vec{v}_i, \vec{r}_i)$ represents the velocity $\vec{v}_i$ and the position $\vec{r}_i$ of particle i ($i = 1, 2, \ldots, N$). The Maxwell-Boltzmann factor $\phi(v_i)$ is

defined as

$$\phi(v) = (m\beta/2\pi)^{3/2}\exp(-\tfrac{1}{2}\beta m v^2) \quad . \tag{2.3}$$

The function W(12...N) represents the statistical correlations between the positions of the particles and is given by

$$W(12...N) = \exp\left[-\beta \sum_{i<j}^{N}\sum U(r_{ij})\right] = \prod_{i<j}^{N}(1+f_{ij}) \, , \tag{2.4}$$

where $U(r_{ij})$ is the pair potential as a function of the relative distance $r_{ij} = |\vec{r}_i - \vec{r}_j|$ and f_{ij} the Mayer function. For a system of hard spheres with diameter σ the statistical correlations reduce to overlap exclusions and the Mayer function reads

$$f_{ij} = W(ij)-1 = -\theta(\sigma-r_{ij}) \, , \tag{2.5}$$

where $\theta(x) = 1$ for $x > 0$ and $\theta(x) = 0$ for $x < 0$.

The expressions (2.1) involve correlation functions between the current J at time t and at time t = 0. For thermal conductivity and viscosity the current consists of a kinetic term J^K and a potential energy term J^U

$$J = J^K + J^U \quad , \tag{2.6}$$

with

$$\begin{aligned} \vec{J}^K_\lambda &= \sum_{i=1}^{N} \vec{J}_\lambda(\vec{v}_i) = \sum_{i=1}^{N} (\tfrac{1}{2}mv_i^2 - \tfrac{5}{2}kT)\vec{v}_i \quad , \\ \vec{\vec{J}}^K_\eta &= \sum_{i=1}^{N} \vec{\vec{J}}_\eta(\vec{v}_i) = \sum_{i=1}^{N} m\{\vec{v}_i\vec{v}_i\}_s \quad ; \end{aligned} \tag{2.7}$$

and

$$\vec{\vec{J}}^{U}_{\lambda} = \frac{1}{2}\sum_{i\neq j}^{N}\sum [U(r_{ij})\vec{\vec{I}}-\vec{r}_{ij}\partial U(r_{ij})/\partial\vec{r}_{ij}]\cdot\vec{v}_i - h^{U}\sum_{i=1}^{N}\vec{v}_i \quad ,$$

$$\vec{\vec{J}}^{U}_{\eta} = -\frac{1}{2}\sum_{i\neq j}^{N}\sum' \{\vec{r}_{ij}\partial U(r_{ij})/\partial\vec{r}_{ij}\}_s \quad . \tag{2.8}$$

The symbol $\{\ \}_s$ indicates a traceless symmetrized tensor, $\vec{\vec{I}}$ is the unit tensor and $h = \frac{5}{2}kT + h^U$ the enthalpy per particle. The self-diffusion contains only a kinetic term, as shown in (2.1).

The separation of the currents in two parts (2.6) implies that λ and η can be considered as the sum of a number of distinct contributions

$$\lambda = \lambda^{KK}+\lambda^{KU}+\lambda^{UK}+\lambda^{UU} \quad ,$$
$$\eta = \eta^{KK}+\eta^{KU}+\eta^{UK}+\eta^{UU} \quad , \tag{2.9}$$

with obvious definitions for the individual terms.

The main text of this report is devoted to a study of the effect of triple collisions on the first density correction to the transport coefficients. For this purpose it is sufficient to consider only the kinetic terms λ^{KK} and η^{KK}. The remaining terms are sometimes referred to as collisional transfer contributions. This terminology is slightly ambiguous, since in the original work of Enskog [7] collisional transfer refers only to $\lambda^{UK}+\lambda^{UU}$ and $\eta^{UK}+\eta^{UU}$. The lowest order contributions from $\lambda^{KU}+\lambda^{UK}$ and $\eta^{KU}+\eta^{UK}$ are proportional to the

density n. They involve the dynamics of two particles only and are fully accounted for by the theory of Enskog. In Appendix A we show how these terms can be derived from a systematic density expansion of the time correlation functions (2.1). The terms λ^{UU} and η^{UU} account for correlations between two pairs of molecules; their leading contributions are proportional to n^2 and are not considered here.

In order to discuss the time dependence of the current J(t) in (2.1) we need to consider the dynamics of N hard spheres. The dynamics of N interacting particles can be represented formally by streaming operators e^{tL_N}, which generate the solutions of the Hamiltonian equations of motion, i.e. $J(t) = e^{tL_N}J(0)$. However, for hard spheres the streaming operators are not defined when the particles are overlapping. On the other hand the streaming operators are always preceded by the function W(12...N) giving zero weight to initially overlapping configurations. One, therefore, has the freedom to extend the definition domains of the streaming operators to include initially overlapping configurations. Pseudo streaming operators e^{tL_N} and $e^{t\bar{L}_N}$, defined for all configurations, which generate for non-overlapping configurations the actual trajectories of N interacting hard spheres, have been introduced by Ernst, Dorfman, Hoegy and Van Leeuwen [14], and will be used in this report. The operators L_N and $\bar{L}_N$ are given by

$$L_N = L_o + \sum_{i<j}^{N}\sum T_{ij} \quad , \qquad \bar{L}_N = L_o + \sum_{i<j}^{N}\sum \bar{T}_{ij} \quad , \tag{2.10}$$

where L_o is the Liouville operator associated with the free streaming of the particles

$$L_o = L_o(12\ldots N) = \sum_{i=1}^{N} \vec{v}_i \cdot \partial/\partial \vec{r}_i \quad , \tag{2.11}$$

and where the operators T_{ij} and $\bar{T}_{ij}$ are associated with a binary collision between particles i and j. The operators T_{ij} and $\bar{T}_{ij}$ contain an interacting and a non-interacting term

$$T_{ij} = T^i_{ij} + T^n_{ij} \quad ; \quad \bar{T}_{ij} = T^i_{ij} + \bar{T}^n_{ij} \quad , \tag{2.12}$$

such that

$$T^i_{ij} = \sigma^2 \int d\hat{\sigma}_{ij} |\vec{v}_{ij} \cdot \hat{\sigma}_{ij}| \delta(\vec{r}_{ij} - \vec{\sigma}_{ij}) R_{\sigma_{ij}} \tag{2.12a}$$

$$\vec{v}_{ij} \cdot \hat{\sigma}_{ij} < 0$$

describes an <u>interacting</u> collision,

$$T^n_{ij} = -\sigma^2 \int d\hat{\sigma}_{ij} |\vec{v}_{ij} \cdot \hat{\sigma}_{ij}| \delta(\vec{r}_{ij} - \vec{\sigma}_{ij}) \tag{2.12b}$$

$$\vec{v}_{ij} \cdot \hat{\sigma}_{ij} < 0$$

describes a <u>non-interacting penetrating</u> collision, and

$$\bar{T}^n_{ij} = -\sigma^2 \int d\hat{\sigma}_{ij} |\vec{v}_{ij} \cdot \hat{\sigma}_{ij}| \delta(\vec{r}_{ij} - \vec{\sigma}_{ij}) \tag{2.12c}$$

$$\vec{v}_{ij} \cdot \hat{\sigma}_{ij} > 0$$

describes a <u>non-interacting separating</u> collision. The symbol

$\hat{\sigma}_{ij} = \vec{\sigma}_{ij}/\sigma$ represents a unit vector (perihelion vector of the collision) and the operator $R_{\sigma_{ij}}$ transforms the velocities $\vec{v}_i$ and $\vec{v}_j$ *before* the collision into the velocities $\vec{v}_i^*$ and $\vec{v}_j^*$ *after* the collision†

$$
\begin{aligned}
R_{\sigma_{ij}} \vec{v}_i &= \vec{v}_i^* = \vec{v}_i - (\vec{v}_{ij} \cdot \hat{\sigma}_{ij}) \hat{\sigma}_{ij} \quad , \\
R_{\sigma_{ij}} \vec{v}_j &= \vec{v}_j^* = \vec{v}_j + (\vec{v}_{ij} \cdot \hat{\sigma}_{ij}) \hat{\sigma}_{ij} \quad , \\
R_{\sigma_{ij}} \vec{v}_k &= \vec{v}_k \qquad (i \neq k \neq j) \quad ,
\end{aligned}
\tag{2.13}
$$

where $\vec{v}_{ij} = \vec{v}_i - \vec{v}_j$. Equations (2.13) describe the "hard sphere interaction" in which molecules i and j exchange velocity components along the perihelion vector $\vec{\sigma}_{ij}$.

To illustrate the meaning of these different types of binary collisions we consider in Fig. 1 the motion of particle 1 relative to particle 2. At a given time $\tau = 0$ particle 1 is approaching particle 2 with a relative velocity $\vec{v}_{12}$ and an impact parameter $b_{12} < \sigma$. After a time $\tau = \tau_{12}^-$ the center of 1 will touch the interaction sphere of 2 at A $(\vec{v}_{12} \cdot \sigma_{12} < 0)$. If the collision is an interacting one, particle 1 will proceed along its deflected path in the direction of $\vec{v}_{12}^*$. If the collision is non-interacting penetrating, particle 1 will continue to move in the direction of $\vec{v}_{12}$. In the latter case the particles will experience a non-interacting separating collision after a time $\tau = \tau_{12}^+$,

†In this report we use *forward* streaming operators in contrast to a previous publication on this subject [12].

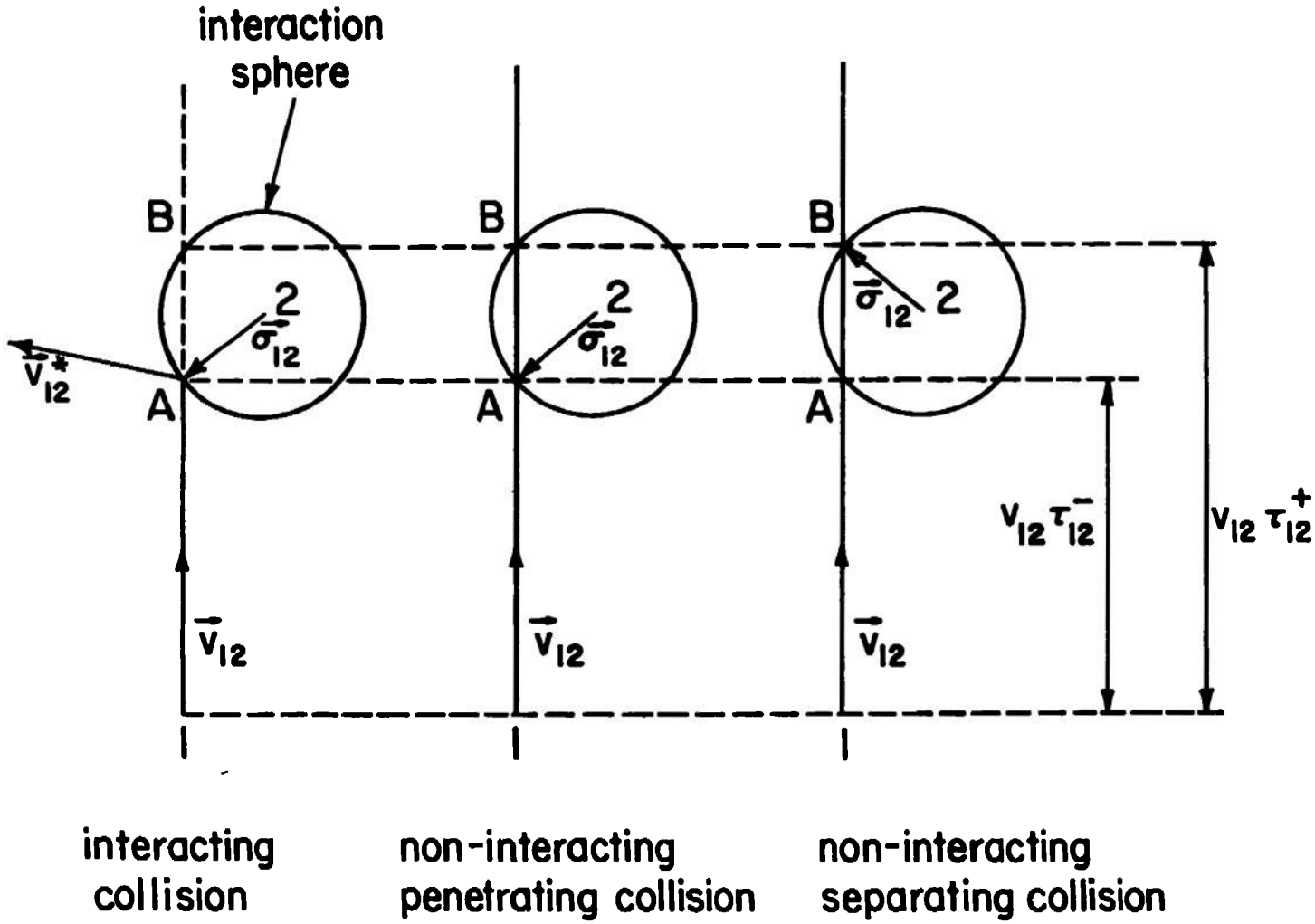

Fig. 1. Geometry of a collision between two hard spheres.

when particle 1 touches the interaction sphere of 2 at B ($\vec{v}_{12}\cdot\hat{\sigma}_{12}>0$).

Since the transport coefficients (2.1) are Laplace transforms of the time correlation functions, it is convenient to take the Laplace transform of the pseudo-streaming operators (resolvent operators)

$$G_N = \left[\varepsilon - L_N\right]^{-1}, \qquad \bar{G}_N = \left[\varepsilon - \bar{L}_N\right]^{-1}, \qquad G_o = \left[\varepsilon - L_o\right]^{-1} . \tag{2.14}$$

We shall not indicate explicitly that L_o and G_o are N-particle operators. Both streaming operators e^{tL_N} and $e^{t\bar{L}_N}$ or G_N and $\bar{G}_N$ describe the hard sphere dynamics correctly, provided they are used in the appropriate combination with the overlap exclusion. That is, the operator e^{tL_N} represents the dynamics correctly when written *behind* the overlap exclusion W(12....N) and the operator $e^{t\bar{L}_N}$ when written *in front of* W(12....N). Thus, the allowed combinations are

$$W(12...N)e^{tL_N} = e^{t\bar{L}_N}W(12...N) , \tag{2.15a}$$

or

$$W(12...N)G_N = \bar{G}_N W(12...N) . \tag{2.15b}$$

After this review of hard sphere dynamics, the kinetic contributions to the transport coefficients will be related to one-particle fluxes $J(\vec{v})$ by integrating the time correlation functions (2.1) over the positions of N particles and

the velocities of N-1 particles [4]

$$\lambda^{KK} = \frac{n}{3kT^2}\int d\vec{v}\phi(v)\vec{J}_\lambda(\vec{v})\cdot\vec{\Psi}_\lambda(\vec{v};0) \quad ,$$

$$\eta^{KK} = \frac{n}{10kT}\int d\vec{v}\phi(v)\overleftrightarrow{J}_\eta(\vec{v}):\overleftrightarrow{\Psi}_\eta(\vec{v};0) \quad , \qquad (2.16)$$

$$nD = \frac{1}{3}n\int d\vec{v}\phi(v)\vec{v}\cdot\vec{\Psi}_D(\vec{v};0) \quad .$$

We represent the functions $\Psi(\vec{v};0) = \lim_{\varepsilon\to 0}\Psi(\vec{v};\varepsilon)$ as the result of an operator $\Gamma(\vec{v};\varepsilon)$ operating on the appropriate flux $J(\vec{v})$

$$\vec{\Psi}_\lambda(\vec{v};\varepsilon) = \Gamma(\vec{v};\varepsilon)\vec{J}_\lambda(\vec{v}) \quad , \qquad \overleftrightarrow{\Psi}_\eta(\vec{v};\varepsilon) = \Gamma(\vec{v};\varepsilon)\overleftrightarrow{J}_\eta(\vec{v}) \quad . \qquad (2.17)$$

Then it follows from (2.1) that

$$n\Gamma(\vec{v}_1;\varepsilon) = \lim_{V\to\infty}\sum_N \frac{z^N}{(N-1)!Z}\int dx^{N-1}\prod_{i=2}^{N}\phi(v_i)W(12\ldots N)G_N\sum_{j=1}^{N}P_{1j} \quad . \qquad (2.18)$$

The operator P_{1j} in (2.18) is a permutation operator which interchanges the labels of particles 1 and j. The corresponding relation for the self-diffusion reads

$$\vec{\Psi}_D(\vec{v};\varepsilon) = \tilde{\Gamma}(\vec{v};\varepsilon)\vec{v} \quad , \qquad (2.17c)$$

where $\tilde{\Gamma}(\vec{v};\varepsilon)$ is obtained from (2.18) by deleting the sum of the permutation operators.

In order to obtain an integral equation for the functions Ψ in (2.17) we follow a method proposed by Zwanzig [15]. A cluster expansion of the resolvent operators leads to a formal

density expansion for the operator $\Gamma(\vec{v};\varepsilon)$. Next, we determine the density expansion of Γ^{-1}, and multiply (2.17) with the inverse operator Γ^{-1} to obtain the desired integral equation.

For this purpose we introduce a set of N-particle resolvent operators

$$G_N(12...n) = G(12...n) = \left[\varepsilon - L_o(12...N) - \sum_{i}^{n}\sum_{j} T_{ij}\right]^{-1}, \qquad (2.19)$$

in which collisions (T-operators) between only the first n particles ($n \leq N$) are taken into account. Cluster operators are then defined by the recursion relation

$$G(12...n) = \sum_{\ell=1}^{N} \sum_{1\subset[\ell]\subset[n]} U(12...\ell). \qquad (2.20)$$

The second summation is taken over all sets $[\ell]$ of ℓ particles which contain particle 1 and are themselves contained in $[n] = (1...n)$. For example,

$$\begin{aligned} G(1) &= G_o = \{\varepsilon - L_o(12...N\}^{-1} = U(1), \\ G(12) &= U(1)+U(12), \\ G(123) &= U(1)+U(12)+U(13)+U(123). \end{aligned} \qquad (2.20a)$$

Inversion of the recursion relation (2.20) yields

$$U(12...\ell) = \sum_{k=1}^{\ell} (-1)^{\ell-k} \sum_{1\subset[k]\subset[\ell]} G(12...k). \qquad (2.21)$$

In particular, the first few terms read

$$U(1) = G(1) = G_0 \quad ,$$

$$U(12) = G(12) - G_0 \quad , \tag{2.21a}$$

$$U(123) = G(123) - G(12) - G(13) + G_0 .$$

We note that all operators in (2.20) and (2.21) operate on the phases of N particles.

When we introduce this cluster expansion into expression (2.18) for Γ we can start from either $W(12\ldots N)G_N$ or $\bar{G}_N W(12\ldots N)$. In the latter case we define $\bar{U}$-operators by replacing G with $\bar{G}$ in (2.20). Due to (2.15b) both procedures are equivalent, but the second representation is more convenient in view of the integrations over the phases of particles 2 and 3, to be carried out in the next section.

Next, the cluster decomposition (2.20) is substituted in (2.18) to obtain an expansion for the operator

$$\Gamma(\vec{v}_1;\varepsilon) = \sum_{\ell=1}^{\infty} \frac{n^{\ell-1}}{(\ell-1)!} \int dx^{\ell-1} \prod_{i=2}^{\ell} \phi(v_i) \bar{U}(12,..\ell) g(12\ldots\ell) \sum_{j=1}^{\ell} P_{1j}, \tag{2.22}$$

where we have introduced the equilibrium distribution functions $g(12\ldots\ell)$ [16]:

$$n^{\ell} g(12\ldots\ell) = \lim_{V\to\infty} \sum_{N=\ell}^{\infty} \frac{z^N}{(N-\ell)!Z} \int dx^{N-\ell} \prod_{i=\ell+1}^{N} \phi(v_i) W_N \quad , \tag{2.23}$$

with $g(1) = 1$. The reduced distribution functions $g(12\ldots\ell)$ can be represented by a power series in the density. Here we

quote only those terms which we shall need explicitly [16]:

$$g(12) = W(12)+n\int dx_3\phi(v_3)W(12)f_{13}f_{23}+\cdots,$$
$$g(123) = W(123)+\cdots \quad . \tag{2.24}$$

The form (2.22) for the operator Γ is appropriate only when operating on functions $J(\vec{v})$ of the velocity for which

$$\int d\vec{v}\phi(v)J(\vec{v}) = 0, \tag{2.25}$$

and this is precisely the case for the transport coefficients. We note that the operators $\bar{U}(12\ldots\ell)$ in (2.22) now operate only on the phases of ℓ particles. The reason is that the terms operating on the remaining $(N-\ell)$ particles give rise to vanishing surface terms. The operator $\tilde{\Gamma}$ for the self-diffusion is also given by (2.22) provided that we delete again the permutation operators.

We expand the operator Γ in a power series in the density

$$\Gamma = \Gamma_1+n\Gamma_2+n^2\Gamma_3+\cdots \quad , \tag{2.26}$$

with

$$\Gamma_1 = G_o \quad , \tag{2.26a}$$

$$\Gamma_2 = \int dx_2\phi(v_2)\bar{U}(12)W(12)\sum_{i=1}^{2}P_{1i} \quad , \tag{2.26b}$$

$$\Gamma_3 = \int dx_2dx_3\phi(v_2)\phi(v_3)\{\tfrac{1}{2}\bar{U}(123)W(123)+\bar{U}(12)W(12)f_{13}f_{23}\}\sum_{i=1}^{3}P_{1i}. \tag{2.26c}$$

In order to write Γ_3 in the form (2.26c) we have added a term $\bar{U}(12)W(12)f_{13}f_{23}P_{13}$ which vanishes after integration over $\vec{v}_3$ according to (2.25). Again the corresponding terms for the expansion of $\tilde{\Gamma}$ are obtained by deleting the permutation operators.

As pointed out by Zwanzig [15] the density expansion (2.26) is not suitable for a calculation of the functions $\Psi(\vec{v};\varepsilon)$ in (2.17), since the coefficients Γ_k of the expansion diverge as ε^{-k} in the limit $\varepsilon\to 0$. However, Zwanzig has also shown that the inverse operator $\Gamma^{-1}(\varepsilon)$ has a finite limit as $\varepsilon\to 0$, at least for the first three terms in the density expansion of $\Gamma^{-1}(\varepsilon)$. This leads us, after inverting (2.26) and performing a density expansion, to the following integral equations for $\Psi(\vec{v};\varepsilon)$:

$$J(\vec{v}) = \lim_{\varepsilon\to 0}\Gamma^{-1}(\vec{v};\varepsilon)\Psi(\vec{v};\varepsilon) = -\{nI_2(\vec{v})+n^2I_3(\vec{v})+\ldots\}\Psi(\vec{v};0), \qquad (2.27)$$

with

$$I_2(\vec{v}) = \lim_{\varepsilon\to 0}G_o^{-1}\Gamma_2(\vec{v};\varepsilon)G_o^{-1}, \qquad (2.28a)$$

$$I_3(\vec{v}) = \lim_{\varepsilon\to 0}\{G_o^{-1}\Gamma_3(\vec{v};\varepsilon)G_o^{-1}-G_o^{-1}\Gamma_2(\vec{v};\varepsilon)G_o^{-1}\Gamma_2(\vec{v};\varepsilon)G_o^{-1}\}. \qquad (2.28b)$$

The operator G_o^{-1} can be replaced with ε when acting on functions of the velocities alone. In deriving (2.27) we have used the property that $\lim_{\varepsilon\to 0}G_o^{-1}\Psi(\vec{v};\varepsilon) = \lim_{\varepsilon\to 0}\varepsilon\Psi(\vec{v};\varepsilon) = 0$.

The operator $I_2(\vec{v})$ is the Boltzmann collision operator which will be reduced to its familiar form in the next section; the operator $I_3(\vec{v})$ is a triple collision operator. In the integral equations (2.27) both operators act on a

function of the velocity alone. For the self-diffusion we obtain similarly the integral equation

$$\vec{v} = -\{n\tilde{I}_2(\vec{v})+n^2\tilde{I}_3(\vec{v})+\cdots\}\vec{\Psi}_D(\vec{v};0), \tag{2.29}$$

where the operators $\tilde{I}_k(\vec{v})$ are given by (2.28) after replacing Γ_k with $\tilde{\Gamma}_k$.

The solution $\Psi(\vec{v};0)$ of the integral equation (2.27) can be written in the form of a density expansion

$$\Psi(\vec{v};0) = -n^{-1}\{I_2^{-1}-nI_2^{-1}I_3I_2^{-1}+\cdots\}J(\vec{v}) , \tag{2.30}$$

and a similar result follows from (2.29). When the formal solution (2.30) is inserted into (2.16), we obtain a density expansion for the kinetic parts of the transport coefficients

$$\begin{aligned} \lambda^{KK} &= \lambda_o+\lambda_1^{KK}n+\cdots , \\ \eta^{KK} &= \eta_o+\eta_1^{KK}n+\cdots , \\ nD &= D_o+D_1n+\cdots . \end{aligned} \tag{2.31}$$

The lowest density contributions are in general of the form

$$-\int d\vec{v}\phi(\vec{v})J(\vec{v})I_2^{-1}(\vec{v})J(\vec{v}) , \tag{2.32a}$$

while the first order density corrections have the form

$$\int d\vec{v}\phi(v)J(\vec{v})I_2^{-1}I_3I_2^{-1}J(\vec{v}), \tag{2.32b}$$

as follows from (2.16) and (2.30).

In order to express the quantities (2.32) as matrix elements of collision operators we introduce the functions $\vec{A}$, $\vec{\vec{B}}$ and $\vec{C}$, which are determined by the integral equations

$$I_2(\vec{v})\vec{A}(\vec{v}) = -\vec{J}_\lambda(\vec{v}),$$

$$I_2(\vec{v})\vec{\vec{B}}(\vec{v}) = -\vec{\vec{J}}_\eta(\vec{v}), \qquad (2.33)$$

$$\tilde{I}_2(\vec{v})\vec{C}(\vec{v}) = -\vec{v} \quad .$$

From (2.32), (2.33) and the symmetry of the Boltzmann collision operators I_2, it follows then that the low density values λ_o, η_o and D_o are given by

$$\lambda_o = -\frac{1}{3kT^2}\,[A,A]^{(2)},$$

$$\eta_o = -\frac{1}{10kT}\,[\vec{\vec{B}},\vec{\vec{B}}]^{(2)}, \qquad (2.34)$$

$$D_o = -\frac{1}{3}\,[\vec{C},\vec{C}]^{\tilde{(2)}}.$$

For the first density corrections λ_1^{KK}, η_1^{KK} and D_1 we obtain

$$\lambda_1^{KK} = \frac{1}{3kT^2}\,[\vec{A},\vec{A}]^{(3)},$$

$$\eta_1^{KK} = \frac{1}{10kT}\,[\vec{\vec{B}},\vec{\vec{B}}]^{(3)}, \qquad (2.35)$$

$$D_1 = \frac{1}{3}\,[\vec{C},\vec{C}]^{\tilde{(3)}}.$$

For convenience we have introduced a short hand notation defining matrix elements associated with the operators I_k and $\tilde{I}_k$

$$[f,g]^{(k)} \equiv \int d\vec{v}\phi(v) f(\vec{v}) * I_k(\vec{v}) g(\vec{v}) \tag{2.36a}$$

$$[f,g]^{(\tilde{k})} \equiv \int d\vec{v}\phi(v) f(\vec{v}) * \tilde{I}_k(\vec{v}) g(\vec{v}) \tag{2.36b}$$

where $g(\vec{v})$ and $f(\vec{v})$ are vector or tensor functions of the velocity $\vec{v}$ and $*$ indicates the appropriate scalar product.

III. Dynamics of hard spheres

Once the coefficients in the expansion (1.1) for the transport properties are related to collision operators, the problem is reduced to an analysis of the dynamics of two, three, etc. isolated hard spheres. To describe the dynamics we introduced binary collision operators in (2.12). We now summarize some of the properties of the T-operators and elucidate how they enable us to give a compact and systematic description of collision sequences.

The T-operators correspond to binary collisions which may be interacting or non-interacting. The G_o-operators, defined in (2.14), correspond to free streaming of the particles. Products of T-operators and G_o-operators correspond to sequences of successive binary collisions among the particles, and can be represented by diagrams. The G_o-operators are represented by labeled particle lines (labels 1,2,3) indicating the free trajectories of the particles between collisions. We adopt the convention that time increases when the diagrams are read from bottom to top as indicated by arrows on the particle lines. The T-operators correspond to the basic binary collision events and are represented schematically in Fig. 2. The collisions are assumed to occur at a given time $\tau = \tau_o$ and in Fig 2a we indicate that the velocities change in an interacting collision. In Fig. 2b and 2c the velocities do not change,

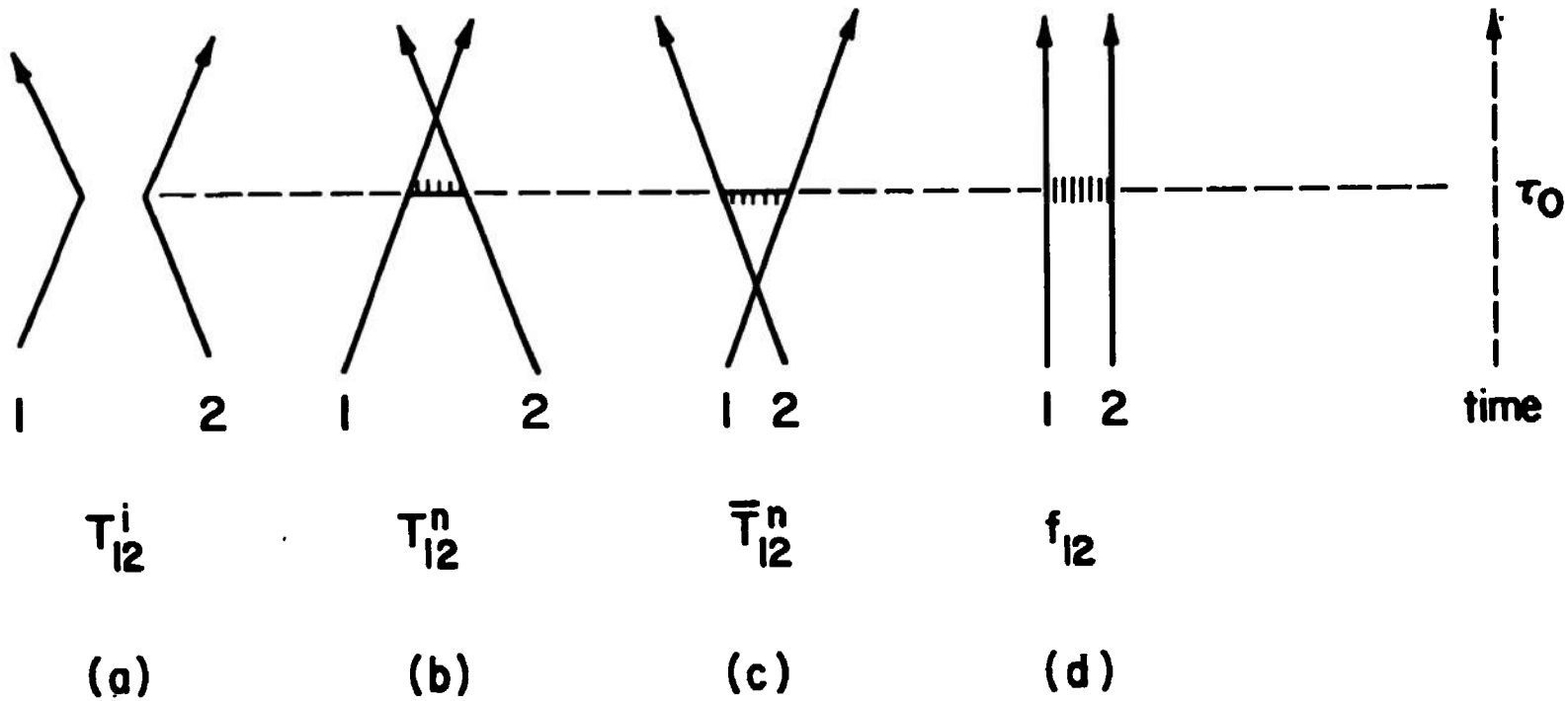

Fig. 2. Schematic representation of (a) an interacting collision, (b) a non-interacting penetrating collision, (c) a non-interacting separating collision, and (d) the condition that the two particles overlap at time $\tau=\tau_0$.

but we place marks just above/below the collision time in the non-interacting penetrating/separating collision to indicate that the particles overlap just after/before the collision. Occasionally, it will be necessary to require that the particles overlap at a given time $\tau = \tau_o$; we do this by connecting their trajectories with marks as shown in Fig. 2d.

Using the foregoing symbolic representation, we can construct diagrams representing *sequences* of collisions. As examples we show in Fig. 3 the diagrams associated with the various terms in the operator products $T_{12}G_oT_{13}$ and $\bar{T}_{12}G_oT_{13}$. The operator T_{12} is only different from zero when particles 1 and 2 are in contact. The operator T_{13} requires that at the same time the phase of particle 3 is such that the collision between 1 and 2 is followed by a collision between 1 and 3, i.e. $\tau_{13}>\tau_{12}$. For interacting and non-interacting penetrating collisions the time ordering refers to τ_α^- and for non-interacting separating collisions to τ_α^+, where α indicates the appropriate pair. The operators act on functions of the positions and velocities of the three molecules. The effect of the operator product is to transform the positions and velocities of the molecules just *prior* to the first collision at the bottom of the diagram into those just *after* the last collision at the top of the diagram†. As mentioned earlier, any penetrating collision will be followed by a separating collision at a

†Notice that the bottom/top of the diagram is determined by the first/last collision. The extensions of the particle lines below the first collision and above the last collision are shown for convenience only; they do not represent G_o-operators.

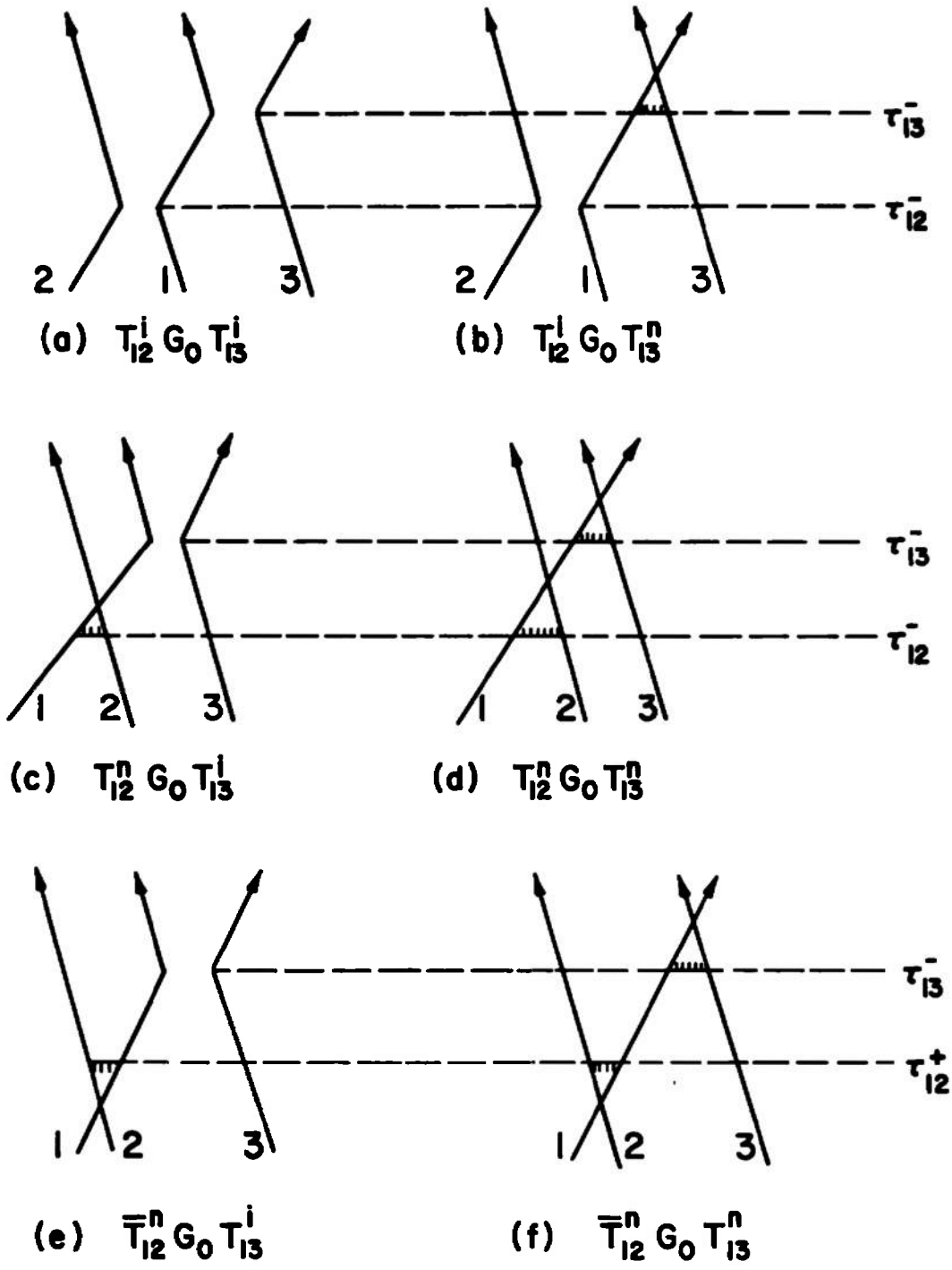

Fig. 3. Collision sequences associated with the operator products $T_{12}G_0T_{13}$ and $\bar{T}_{12}G_0T_{13}$.

later time. However, the diagrams are non-committal about the number of and the time at which additional non-interacting collisions, not indicated explicitly, will occur. For example, in Figs. 3c and 3d a separating collision between 1 and 2 will occur at $\tau = \tau_{12}^{+}$, but τ_{12}^{+} may be either smaller or larger that τ_{13}^{-}. As another example, we show in Fig. 4 the diagrams associated with the two terms of the operator product $f_{23}T_{12}^{i}G_{o}T_{13}$. In these collision sequences particles 1 and 2 are colliding, while 2 overlaps with 3. These diagrams can roughly be thought of as space-time plots of the centers of the molecules, with the time-axis vertical and the (one-dimensional) space-axis horizontal, and they allow a direct geometrical interpretation of the collision operator products.

The operators satisfy a number of properties listed in Table I. Proofs of these relations are either given by Ernst et al. [14] or are directly implied by their results. The relations (I.1) through (I.6) have an obvious dynamical meaning, when interpreted geometrically. In (I.8) the operation of time reversal is represented by the operator $\mathcal{T}$ which reverses the directions of the velocities of all particles, while their positions remain unchanged.

Any product of T- and G_{o}-operators can be interpreted as a specific sequence of collisions. However, some sequences may not be allowed according to the laws of mechanics.

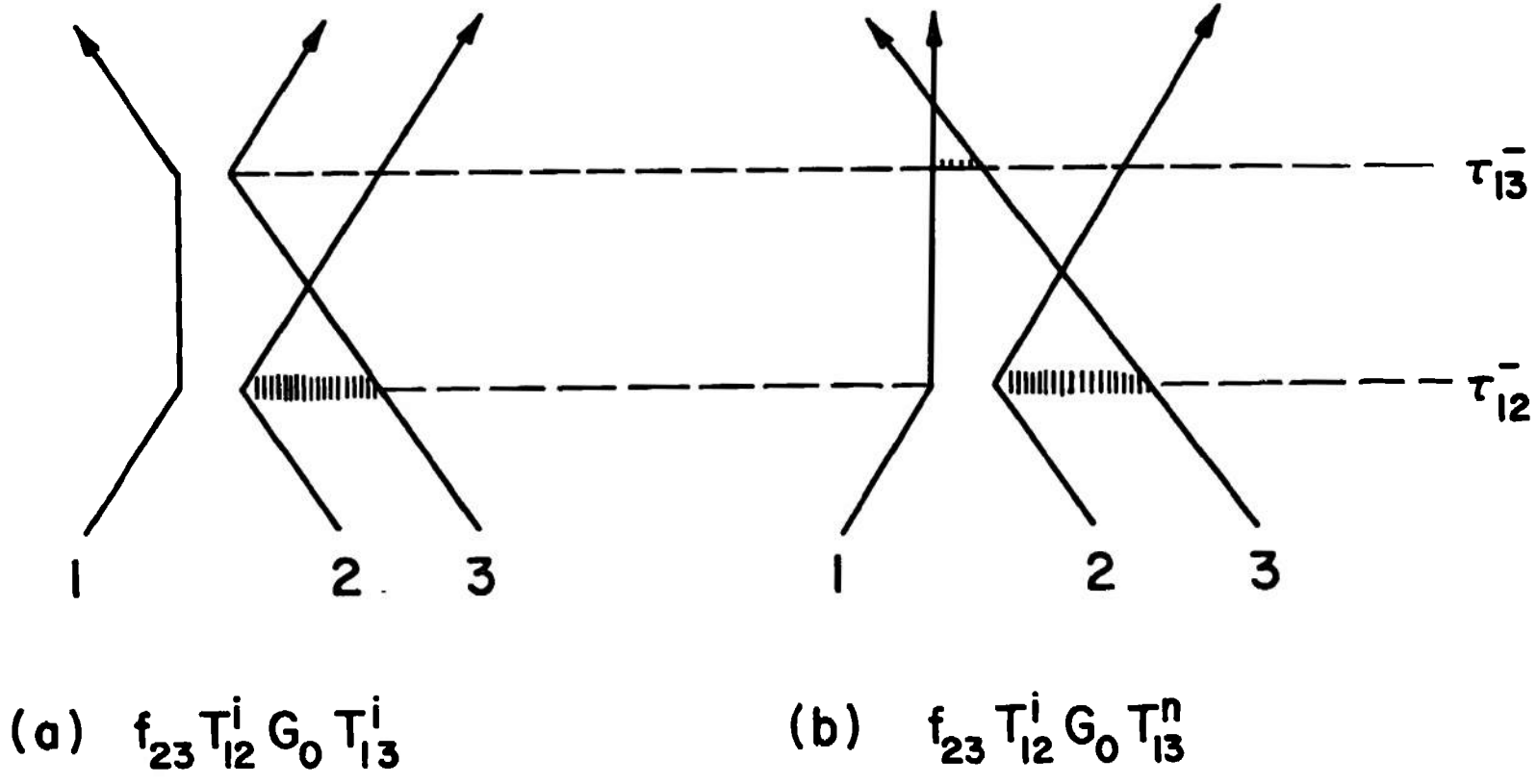

Fig. 4. Collision sequences associated with the operator product $f_{23}T_{12}^{i}G_0T_{13}$.

TABLE I

PROPERTIES OF BINARY COLLISION OPERATORS

$f_\alpha T_\alpha = 0$, $\overline{T}_\alpha f_\alpha = 0$, $f_\alpha G_o T_\alpha = 0$, $\overline{T}_\alpha G_o f_\alpha = 0$ $T_\alpha G_o T_\alpha = 0$, $\overline{T}_\alpha G_o T_\alpha = 0$, $\overline{T}_\alpha G_o \overline{T}_\alpha = 0$ These relations apply also to i- and n-collisions separately. In these relations G_o may be replaced by $G_o T^n_{\alpha_1} G_o \ldots T^n_{\alpha_\ell} G_o$ if $\alpha_i \neq \alpha$ for $i = 1,2\ldots\ell$; in addition any $T^n_{\alpha_i}$ $(\alpha_i \neq \alpha)$ may be replaced by $\overline{T}^n_{\alpha_i}$	I.1
$T_\alpha f_\alpha = -T^n_\alpha$, $f_\alpha \overline{T}_\alpha = -\overline{T}^n_\alpha$	I.2
$f_\alpha T_\beta = T_\beta f_\alpha$, $f_\alpha \overline{T}_\beta = \overline{T}_\beta f_\alpha$ $(\alpha \neq \beta)$	I.3
$f_\alpha G_o + G_o T_\alpha G_o = G_o f_\alpha + G_o \overline{T}_\alpha G_o$ $f_\alpha G_o + G_o T^n_\alpha G_o = G_o f_\alpha + G_o \overline{T}^n_\alpha G_o$	I.4
$f_\alpha G_o = -f_\alpha G_o f_\alpha - f_\alpha G_o \overline{T}^n_\alpha G_o$ $G_o f_\alpha = -f_\alpha G_o f_\alpha - G_o T^n_\alpha G_o f_\alpha$	I.5
$T^n_\alpha G_o = -T^n_\alpha G_o f_\alpha - T^n_\alpha G_o \overline{T}^n_\alpha G_o$ $G_o \overline{T}^n_\alpha = -f_\alpha G_o \overline{T}^n_\alpha - G_o T^n_\alpha G_o \overline{T}^n_\alpha$	I.6
$T_{ij} \begin{bmatrix} 1 \\ \vec{v}_i + \vec{v}_j \\ v_i^2 + v_j^2 \end{bmatrix} = 0$, $\int d\vec{v}_i d\vec{v}_j \begin{bmatrix} 1 \\ \vec{v}_i + \vec{v}_j \\ v_i^2 + v_j^2 \end{bmatrix} \overline{T}_{ij} f(x_i,x_j) = 0$ $\int d\vec{r}_{ij} T_{ij} f(\vec{v}_i,\vec{v}_j) = \int d\vec{r}_{ij} \overline{T}_{ij} f(\vec{v}_i,\vec{v}_j)$ where $f(x_i,x_j)$ and $f(\vec{v}_i,\vec{v}_j)$ are arbitrary functions.	I.7
$T^\dagger_\alpha = T \overline{T}_\alpha T^{-1}$, $\overline{T}^\dagger_\alpha = T T_\alpha T^{-1}$ The dagger represents hermitian conjugation; T is the operation of time reversal.	I.8

Of course, the laws of mechanics are here extended to include the possibility of non-interacting collisions. The definition of the T-operators implies that any operator product associated with a forbidden collision sequence vanishes automatically. Some of these forbidden collision sequences are of a trivial nature and follow from the properties of T_α and $\overline{T}_\alpha$ compiled in Table I. For example, it follows from (I.1) that

$$T_\alpha G_0 T_\beta^n G_0 T_\alpha = 0 \quad . \tag{3.1}$$

This relation expresses the fact that a pair of particles cannot recollide after a collision, unless the trajectory of at least one of the two particles is deflected by an intermediate interacting collision with the third particle.

In addition to such obvious restrictions, there are several restrictions which are not of a trivial nature, but are consequences of theorems concerning the dynamics of three hard spheres. In Table II, we present lemmas that express forbidden collision sequences. These lemmas are consequences of the following two theorems:

THEOREM 1. Three hard spheres (with equal masses and diameters) cannot undergo more than four successive interacting collisions. Moreover, any sequence of four successive interacting collisions is either of the type described by the diagram of Fig. 5, or else obtainable therefrom by inter-

TABLE II

LEMMAS INDICATING FORBIDDEN COLLISION SEQUENCES

$(\alpha \neq \beta \neq \gamma \neq \alpha)$

$f_\gamma \overline{T}_\alpha G_o T_\beta G_o T_\alpha = 0$	II.1
$f_\gamma \overline{T}_\alpha G_o T_\beta G_o T_\gamma = 0$	II.2
$\overline{T}_\alpha G_o T_\beta G_o T_\alpha^n G_o f_\alpha T_\gamma = 0$	II.3
$\overline{T}_\alpha G_o T_\beta G_o T_\alpha G_o T_\beta = 0$	II.4
$\overline{T}_\alpha G_o T_\beta G_o T_\gamma G_o T_\alpha = 0$	II.5
$\overline{T}_\alpha G_o T_\beta G_o T_\alpha G_o T_\gamma G_o T_\alpha = 0$	II.6
$\overline{T}_\alpha G_o T_\beta G_o T_\gamma G_o T_\beta G_o T_\alpha = 0$	II.7

The lemmas hold for the interacting and non-interacting terms of each T - or $\overline{T}$ -operator separately. The lemmas remain valid upon insertion of any number of additional T^n - or $\overline{T}^n$ - operators. Moreover, $\overline{T}_\alpha$ may be replaced by T_α.

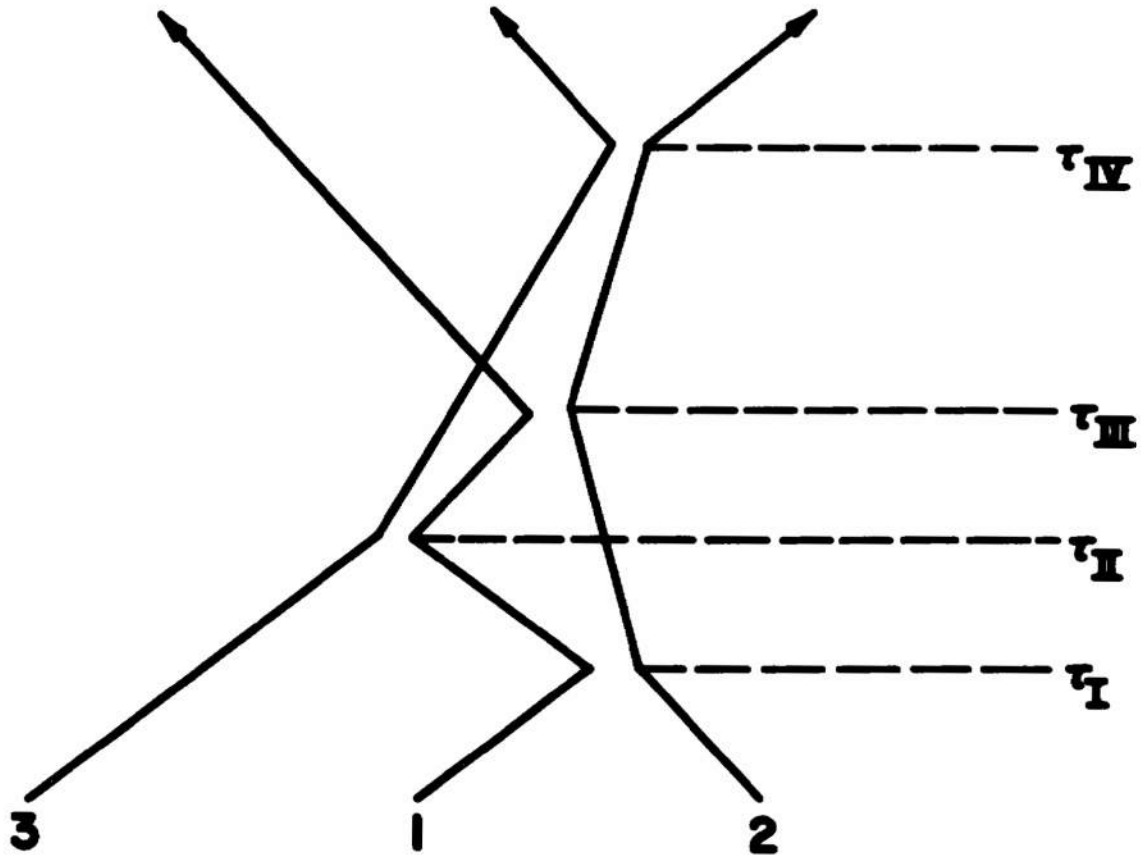

Fig. 5. The only dynamically possible sequence of four successive interacting collisions for three identical hard spheres.

changing particle lables and/or reversing the direction of time.

THEOREM 2. In the recollision sequence defined by the diagram of Fig. 6, it is not possible for spheres 2 and 3 to collide or overlap at any intermediate time: i.e. $r_{32}(\tau)>\sigma$ for $\tau_I^- \leq \tau \leq \tau_{III}^+$.

Theorem 1 was stated by Sandri and coworkers [17] and proved by Murphy and Cohen [18]. Theorem 2 was proved by Hoegy and Sengers [12]. For further details the reader is referred to AEDC-TR-71-51 [11].

In addition to the concepts already used in describing the mechanics of hard sphere collisions, it is convenient to introduce the notion of "overlap collisions", in order to distinguish between statistical and dynamical correlations. An overlap collision is a collision of any type (i.e. interacting, penetrating or separating) between two particles which occurs while at least one of the two colliding particles overlaps with the third particle. The collision between 1 and 2 in Fig. 4 is an example of such an overlap collision. The collision between 1 and 3 in Figs. 3c and 3d would be an overlap collision in the case $\tau_{12}^+ > \tau_{13}^-$. We may further distinguish between single-overlap collisions and double-overlap collisions. In a *single-overlap* collision only *one* of the two colliding particles overlaps with the third

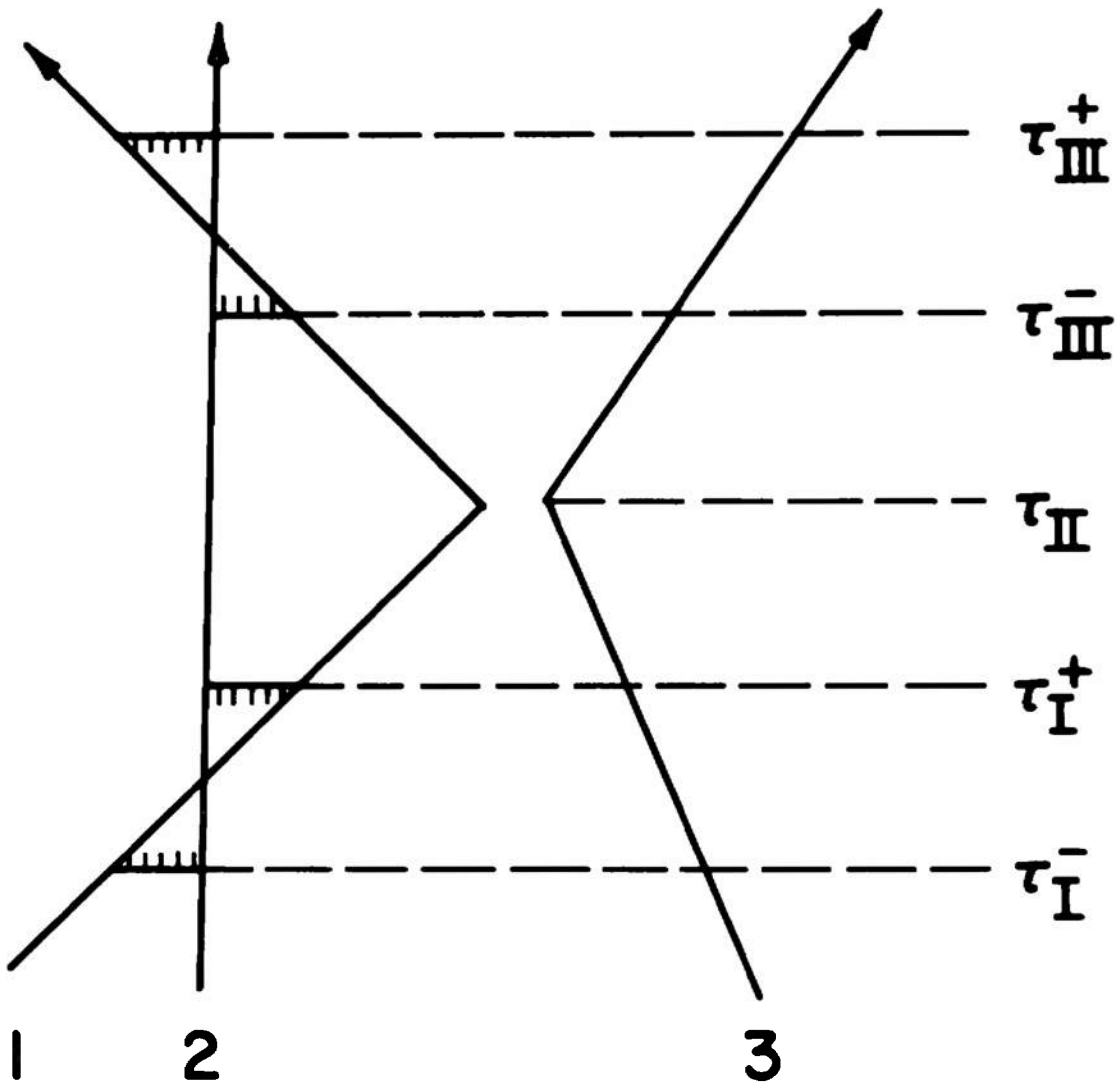

Fig. 6. Recollision sequence for Theorem 2.

particle and in a *double overlap* collision *both* colliding particles overlap with the third particle.

IV. Expansion of the collision operators.

The coefficients of the density expansion for the transport properties are determined by matrix elements or collision integrals (2.34) and (2.35) which involve the collision operators I_2 and I_3, given by (2.28). In this section we show how these collision operators can be decomposed into terms that correspond to collision sequences involving increasing numbers of successive binary collisions.

For this purpose we recall that the collision operators I_2 and I_3 are related to the resolvent operators G(12) and G(123) via (2.26) and (2.21). From (2.19) it follows that the resolvent operators satisfy the integral equations

$$G(12\ldots\ell) = G_o + G_o \sum_{\alpha}' T_\alpha G(12\ldots\ell) \quad , \tag{4.1}$$

where α runs over all pairs among the ℓ particles. A binary collision expansion is obtained upon interation of (4.1)

$$G(12\ldots\ell) = \sum_{s=0}^{\infty} \Big[\sum_{\alpha}' G_o T_\alpha \Big]^s G_o \quad . \tag{4.2}$$

In particular

$$G(12) = G_o + G_o T_{12} G_o \quad . \tag{4.3}$$

In equations (4.1) - (4.3) the operators G and T may be replaced by $\overline{G}$ and $\overline{T}$, respectively. We also note that those terms in (4.2) with two successive T-operators with the same index α vanish automatically as a result of (I.1). This is also

the reason why (4.3) terminates after the second term.

We first consider the Boltzmann collision operator $I_2(\vec{v})$. If we now substitute equation (4.3) for $\bar{G}(12)$ into the expressions (2.28a) for $I_2(\vec{v})$, using (2.26b) and (2.21a), we obtain

$$I_2(\vec{v}_1) = \int dx_2 \phi(v_2) \bar{T}_{12}(1+P_{12}) =$$
$$= \int d\vec{v}_2 \phi(v_2) \sigma^2 \int_{\vec{v}_{12}\cdot\hat{\sigma}_{12} < 0} d\hat{\sigma}_{12} |\vec{v}_{12}\cdot\hat{\sigma}_{12}| (R_{\sigma_{12}} - 1)(1+P_{12}) \quad , \tag{4.4}$$

which is the familiar form of the Boltzmann collision operator. The operator $\tilde{I}_2(\vec{v}_1)$ for the self-diffusion is obtained from (4.4) by deleting the permutation operator P_{12}.

In order to derive a similar expression for the triple collision operator $I_3(\vec{v})$ it is convenient to symmetrize over the labels 2 and 3 in (2.26c). If we then insert (2.21) and iterate (4.1) once, we obtain from (2.28b) after rearranging some terms

$$I_3(\vec{v}_1) = \frac{1}{2} \int dx_2 dx_3 \phi(v_2)\phi(v_3) T(123) \sum_{i=1}^{3} P_{1i} \quad , \tag{4.5}$$

with

$$T(123) = \lim_{\varepsilon \to 0} \Big[\sum_{\alpha_1} \bar{T}_{\alpha_1} \bar{G}(123) W(123) - \sum_{\alpha_1} \bar{T}_{\alpha_1} G_o + \\ - \sum_{\alpha_1 \neq \alpha_2} \sum (\bar{T}_{\alpha_1} G_o f_{\alpha_2} + \bar{T}_{\alpha_1} G_o \bar{T}_{\alpha_2} G_o) \Big] G_o^{-1} \quad . \tag{4.6}$$

The indices α_1 and α_2 in the summations run over the pairs (12), (13) and (23). To obtain a symmetric expression we have added terms starting with $\overline{T}_{23}$ and terms ending with $T_{ij}P_{1k}$ $(k\neq i,j)$; they vanish as a result of (I.7). For the self-diffusion one derives similarly

$$\tilde{I}_3(\vec{v}_1) = \frac{1}{2}\int dx_2 dx_3 \phi(v_2)\phi(v_3)T(123), \tag{4.7}$$

where T(123) is again given by (4.6). As a next step we replace $\overline{G}(123)W(123)$ by $W(123)G(123)$ according to (2.15b) for N=3 and insert the expansion (4.2) for G(123). After rearranging terms and using (I.1) and (I.4) we find [12]

$$T(123) = \sum_{\substack{\alpha_1 \\ (\alpha_1\neq\beta\neq\gamma\neq\alpha_1)}} f_\beta f_\gamma \overline{T}_{\alpha_1} + \sum_{\substack{\alpha_1\neq\alpha_2 \\ (\alpha_1\neq\gamma\neq\alpha_2)}}\sum f_\gamma \overline{T}_{\alpha_1} G_o T_{\alpha_2} + \tag{4.8}$$

$$+ \sum_{\substack{\alpha_1\neq\alpha_2 \\ (\alpha_1\neq\gamma\neq\alpha_2)}}\sum (1+f_\gamma)\overline{T}_{\alpha_1} G_o T_{\alpha_2} \sum_{\ell=1}^{\infty}\Big[\sum_{\alpha_i} G_o T_{\alpha_i}\Big]^{\ell}$$

Some of the conditions on the summations in (4.8) are automatically satisfied due to (I.1). It is always understood that the limit $\varepsilon\to 0$ has to be taken at the end of the calculations, but we omit indicating this limit explicitly.

Expansion (4.8) still contains many terms corresponding to collision sequences that are not allowed by the laws of mechanics. In the last term of the right hand side of (4.8) the term with f_γ vanishes as a result of lemmas (II.1) and

(II.2). This means that the conditions imposed by the presence of $(1+f_\gamma)$ are automatically satisfied. Furthermore, lemmas (II.4) - (II.7) imply that the expansion terminates after products of four T-operators. Thus

$$T(123) = \sum_\alpha f_\beta f_\gamma \bar{T}_\alpha + \sum_\alpha \sum_\beta f_\beta \bar{T}_\alpha G_o T_\gamma + \sum_\alpha \sum_\beta \left[\bar{T}_\alpha G_o T^i_\beta G_o T_\alpha + \bar{T}_\alpha G_o T_\beta G_o T_\gamma \right] + \sum_\alpha \sum_\beta \left[\bar{T}_\alpha G_o T^i_\beta G_o T_\alpha G_o T_\gamma + \bar{T}_\alpha G_o T_\beta G_o T^i_\gamma G_o T_\beta \right] , \tag{4.9}$$

where, from now on, we use the convention $\alpha \neq \beta \neq \gamma \neq \alpha$. In (4.9) we have also omitted those combinations of three or four T-operators which vanish according to (I.1).

As mentioned in the introduction we want to make a distinction between statistical correlations and dynamical correlations. Statistical correlations are determined by those points in configuration space for which two or more particles are overlapping. In the expansion of the collision operators they lead to the presence of "overlap collisions". Therefore, we want to separate the collision sequences into collision sequences with and without overlap collisions. The expansion (4.9), however, is not yet in a form which makes this distinction evident. The reason is that only those configurations for which the particles overlap at the time of the first collision are indicated explicitly in (4.9) by Mayer functions. In addition, however, the collision

sequences may also generate overlap collisions at a later time, not indicated explicitly in (4.9). Such overlap collisions will occur, if a particle has penetrated a second particle and collides with a third particle before it separates from the second particle. Thus we consider in more detail those collision sequences in (4.9) which contain an intermediate T^n- operator. The formal analysis is most easily carried out by using (I.6), which leads to the following decompositions.

$$\bar{T}_\alpha G_o T^n_\beta G_o T_\gamma = -\bar{T}_\alpha G_o T^n_\beta G_o \bar{T}^n_\beta G_o T_\gamma - \bar{T}_\alpha G_o T^n_\beta G_o f_\beta T_\gamma \quad , \tag{4.10}$$

$$\bar{T}_\alpha G_o T^i_\beta G_o T^n_\alpha G_o T_\gamma = -\bar{T}_\alpha G_o T^i_\beta G_o T^n_\alpha G_o \bar{T}^n_\alpha G_o T_\gamma - \bar{T}_\alpha G_o T^i_\beta G_o T^n_\alpha G_o f_\alpha T_\gamma \quad , \tag{4.11a}$$

$$\bar{T}_\alpha G_o T^n_\beta G_o T^i_\gamma G_o T_\beta = -\bar{T}_\alpha G_o T^n_\beta G_o \bar{T}^n_\beta G_o T^i_\gamma G_o T_\beta - \bar{T}_\alpha G_o T^n_\beta G_o f_\beta T^i_\gamma G_o T_\beta \quad . \tag{4.11b}$$

The terms in (4.11) represent sequences of four successive collisions. The last term in (4.11a) vanishes due to lemma (II.3) and the last term in (4.11b) vanishes as a result of (I.1). Since the remaining terms on the right hand side of (4.11) do not contain any Mayer functions, we thus conclude that sequences of four successive collisions cannot lead to any overlap collisions [11,19]. If we substitute (4.10) and (4.11) into (4.9) we obtain the following expansion of the

collision operator

$$T(123) = \sum_{\mu=1}^{4} T_\mu(123) \quad , \tag{4.12}$$

with

$$T_1(123) = \sum_{\alpha} T_E(\alpha) \equiv \sum_{\alpha} f_\beta f_\gamma \overline{T}_\alpha \quad , \tag{4.13}$$

$$T_2(123) = \sum_{\alpha}\sum_{\beta} T_S(\alpha,\beta) \equiv \sum_{\alpha}\sum_{\beta} \overline{T}_\alpha \{f_\gamma G_o - G_o T^n_\gamma G_o f_\gamma\} T_\beta \tag{4.14}$$

$$T_3(123) = \sum_{\alpha}\sum_{\beta} \left[T_R(\alpha,\beta) + T_C(\alpha,\beta) + T_H(\alpha,\beta) \right] \equiv$$

$$\equiv \sum_{\alpha}\sum_{\beta} \left[\overline{T}_\alpha G_o T^i_\beta G_o T_\alpha + \overline{T}_\alpha G_o T^i_\beta G_o T_\gamma - \overline{T}_\alpha G_o T^n_\beta G_o \overline{T}^n_\beta G_o T_\gamma \right] \quad , \tag{4.15}$$

$$T_4(123) = \sum_{\alpha}\sum_{\beta} \left[T_{RC}(\alpha,\beta) + T_{CR}(\alpha,\beta) + T_{RH}(\alpha,\beta) + T_{HR}(\alpha,\beta) \right] \equiv$$

$$\equiv \sum_{\alpha}\sum_{\beta} \Big[\overline{T}_\alpha G_o T^i_\beta G_o T^i_\alpha G_o T_\gamma + \overline{T}_\alpha G_o T^i_\beta G_o T^i_\gamma G_o T_\beta +$$

$$- \overline{T}_\alpha G_o T^i_\beta G_o T^n_\alpha G_o \overline{T}^n_\alpha G_o T_\gamma - \overline{T}_\alpha G_o T^n_\beta G_o \overline{T}^n_\beta G_o T^i_\gamma G_o T_\beta \Big] \, . \tag{4.16}$$

The first term $T_E(\alpha) = f_\beta f_\gamma \overline{T}_\alpha$ requires that pair α collides while both molecules are overlapping with the third molecule. It contains the dynamics of only *one* collision, which is evidently a "double overlap" collision. This term is precisely the term given by the theory of Enskog as will be demonstrated in the next section. We therefore refer to this term as the *double overlap* or *Enskog* term.

To elucidate the meaning of the second term it is advantageous to write it as the sum of three terms, using (I.5),

$$T_S(\alpha,\beta) = T_{SS}(\alpha,\beta)+T_{SN}(\alpha,\beta)+T_{NS}(\alpha,\beta) \equiv$$

$$\equiv -\bar{T}_\alpha\{f_\gamma G_o f_\gamma + f_\gamma G_o \bar{T}_\gamma^n G_o + G_o T_\gamma^n G_o f_\gamma\}T_\beta \qquad (4.17)$$

This term contains the dynamics of *two* successive collisions involving respectively pair α and pair β. In the term $T_{SS}(\alpha,\beta)$ the first and last collisions are single overlap collisions, while $T_{SN}(\alpha,\beta)$ or $T_{NS}(\alpha,\beta)$ corresponds to the case where the first collision is a single overlap collision and the last collision is a non-overlapping collision, or vice versa. We therefore refer to term $T_S(\alpha,\beta)$ as the *single overlap* term.

The terms in $T_3(123)$, given by (4.15), represent sequences of *three* successive collisions to which we refer as *recollisions*, *cyclic collisions* and *hypothetical collisions*. The terms in $T_4(123)$ represent sequences of *four* successive collisions, which are combinations of recollisions, cyclic collisions and hypothetical collisions. We emphasize that both $T_3(123)$ and $T_4(123)$ do not contain any overlap collisions. The geometrical meaning of the various collision sequences will be elucidated in the next section.

The triple collision operator $I_3(\vec{v})$, which is related to T(123) via (4.5), is a *symmetric* operator [11,12]. To exhibit the symmetry we take the hermitian conjugate of the operator T(123). Using (I.8) and the relation $G_o^\dagger = \mathcal{T} G_o \mathcal{T}^{-1}$ we find for the Enskog term

$$T_E^\dagger = f_\beta f_\gamma T T_\alpha T^{-1} \quad , \tag{4.18}$$

and after appropriate relabeling of the particles

$$\begin{aligned} T_{SS}^\dagger(\alpha,\beta) &= T T_{SS}(\alpha,\beta) T^{-1} \quad , \\ T_{SN}^\dagger(\alpha,\beta) &= T T_{NS}(\alpha,\beta) T^{-1} \quad , \end{aligned} \tag{4.19}$$

$$\begin{aligned} T_R^\dagger(\alpha,\beta) &= T T_R(\alpha,\beta) T^{-1} \quad , \\ T_C^\dagger(\alpha,\beta) &= T T_C(\alpha,\beta) T^{-1} \quad , \\ T_H^\dagger(\alpha,\beta) &= T T_H(\alpha,\beta) T^{-1} \quad , \end{aligned} \tag{4.20}$$

$$\begin{aligned} T_{RC}^\dagger(\alpha,\beta) &= T T_{CR}(\alpha,\beta) T^{-1} \quad , \\ T_{RH}^\dagger(\alpha,\beta) &= T T_{HR}(\alpha,\beta) T^{-1} \quad . \end{aligned} \tag{4.21}$$

Thus the triple collision operator $I_3(\vec{v})$ is symmetric in the space of functions $f(\vec{v})$ of the velocity which have a definite parity ($\pm$) under the operation of time reversal, i.e.

$$T f(\vec{v}) \equiv f(-\vec{v}) = \pm f(\vec{v}) . \tag{4.22}$$

The functions of interest in calculating matrix elements of above operators (4.18)-(4.21) are the solutions of the linear inhomogeneous integral equations (2.33). These solutions have indeed a definite parity, while the linearized Boltzmann operator $I_2(\vec{v})$ is isotropic in velocity space. The isotropy of $I_3(\vec{v})$ in velocity space ensures that $I_3(\vec{v})$ does not have

any matrix elements between functions of different parity. A proof of the symmetry of the Zwanzig form of the triple collision operator $I_3(\vec{v})$ for a general potential has been given by Ernst [20].

V. Specification of collision integrals

The expansion (4.12) for T(123) implies an expansion for the first density correction (2.35) to the transport coefficients

$$\lambda_1^{KK} = \sum_{\mu=1}^{4} \lambda_{1\mu} = \frac{1}{3kT^2} \sum_{\mu=1}^{4} [\vec{A},\vec{A}]_\mu^{(3)} ,$$

$$\eta_1^{KK} = \sum_{\mu=1}^{4} \eta_{1\mu} = \frac{1}{10kT} \sum_{\mu=1}^{4} [\vec{\vec{B}},\vec{\vec{B}}]_\mu^{(3)} , \qquad (5.1)$$

$$D_1 = \sum_{\mu=1}^{4} D_{1\mu} = \frac{1}{3} \sum_{\mu=1}^{4} [\vec{C},\vec{C}]_\mu^{(\tilde{3})} ,$$

where the matrix elements are obtained from (2.36) and (4.5), if T(123) is replaced by $T_\mu(123)$ as given in (4.12) - (4.16). The functions $\vec{A}(\vec{v})$, $\vec{\vec{B}}(\vec{v})$ and $\vec{C}(\vec{v})$, determined by the Boltzmann equation (2.33), are usually given in the form of a Sonine polynomial expansion [1]. A numerical representation of these functions has been obtained by Brooker and Green [21]. In general, a calculation of the transport coefficients (5.1) requires the evaluation of a set of triple collision matrix elements of the form

$$[\psi,\chi]_\mu^{(3)} = \frac{1}{2} \int d\vec{v}_1 dx_2 dx_3 \Phi(123) \psi(\vec{v}_1) * T_\mu(123) \sum_{i=1}^{3} \chi(\vec{v}_i) ,$$

$$[\psi,\chi]_\mu^{(3)\sim} = \frac{1}{2} \int d\vec{v}_1 dx_2 dx_3 \Phi(123) \psi(\vec{v}_1) * T_\mu(123) \chi(\vec{v}_1) , \qquad (5.2)$$

where we have introduced the shorthand notation

$$\Phi(123) = \phi(v_1)\phi(v_2)\phi(v_3) . \qquad (5.3)$$

It is convenient to symmetrize these integrals by interchanging the velocity variables to yield

$$[\psi,\chi]_{\mu}^{(3)} = \frac{1}{6}\int d\vec{v}_1 dx_2 dx_3 \Phi(123)\sum_{i=1}^{3}\psi(\vec{v}_i)*T_{\mu}(123)\sum_{j=1}^{3}\chi(\vec{v}_j) \quad ,$$
$$[\psi,\chi]_{\mu}^{(\tilde{3})} = \frac{1}{6}\int d\vec{v}_1 dx_2 dx_3 \Phi(123)\sum_{i=1}^{3}\psi(\vec{v}_i)*T_{\mu}(123)\chi(\vec{v}_i) \quad . \tag{5.4}$$

In this section we shall investigate the structure of these collision integrals and elucidate how they are related to specific collision sequences. The collision integrals corresponding to the first term in the expansion (5.1) are obtained by substituting (4.13) into (5.4). Since the three terms of (4.13) yield equal contributions, we may write

$$[\psi,\chi]_{1}^{(3)} = \frac{1}{2}\int d\vec{v}_1 dx_2 dx_3 f_{13} f_{23} \Phi(123)\sum_{i=1}^{2}\psi(\vec{v}_i)*\bar{T}_{12}\sum_{j=1}^{2}\chi(\vec{v}_j) \quad , \tag{5.5}$$

where the terms i=3 and j=3 vanish as a result of (I.7). We note that the operator $\bar{T}_{12}$ contains a δ-function which restricts the distance r_{12} to the value σ. Using the relation

$$\left[\int d\vec{r}_{13} f_{13} f_{23}\right]_{r_{12}=\sigma} = \frac{5}{12}\pi\sigma^3 \quad , \tag{5.6}$$

which is the value of the first density correction to the radial distribution function $g(r_{12})$ at $r_{12} = \sigma$, we conclude

$$[\psi,\chi]_{1}^{(3)} = \frac{5}{12}\pi\sigma^3[\psi,\chi]^{(2)} \quad , \tag{5.7}$$

where $[\psi,\chi]^{(2)}$ is the well known binary collision integral

associated with the Boltzmann equation. For the self-diffusion we find similarly

$$[\psi,\chi]_1^{(\tilde{3})} = \frac{5}{12}\pi\sigma^3[\psi,\chi]^{(\tilde{2})} \quad . \tag{5.8}$$

It thus follows from (5.1) and (2.34) that

$$\begin{aligned} \lambda_{11} &= -\frac{5}{12}\pi\sigma^3\lambda_o \quad , \\ \eta_{11} &= -\frac{5}{12}\pi\sigma^3\eta_o \quad , \\ D_{11} &= -\frac{5}{12}\pi\sigma^3 D_o \quad , \end{aligned} \tag{5.9}$$

which are precisely the contributions predicted by the theory of Enskog [7].

We now turn our attention to the contributions for $\mu=2,3,4$, not contained in Enskog's theory. Since the collision integrals (5.4) are symmetric with respect to permutations of the particle labels, it suffices to evaluate operators $T_\mu(123)$ for one permutation only. Thus

$$\begin{aligned} [\psi,\chi]_\mu^{(3)} &= \int d\vec{v}_1 dx_2 dx_3 \Phi(123) \sum_{i=1}^{2} \psi(\vec{v}_i) * T_\mu(12,13) \sum_{j=1}^{3} \chi(v_j) \quad , \\ [\psi,\chi]_\mu^{(\tilde{3})} &= \int d\vec{v}_1 dx_2 dx_3 \Phi(123) \sum_{i=1}^{2} \psi(v_i) * T_\mu(12,13) \chi(v_i) \quad , \end{aligned} \tag{5.10}$$

where

$$\begin{aligned} T_2(12,13) &= T_{SS}(12,13)+T_{SN}(12,13)+T_{NS}(12,13) \quad , \\ T_3(12,13) &= T_R(12,13)+T_C(12,13)+T_H(12,13) \quad , \\ T_4(12,13) &= T_{RC}(12,13)+T_{CR}(12,13)+T_{RH}(12,13)+T_{HR}(12,13) \quad , \end{aligned} \tag{5.11}$$

as defined by (4.14)-(4.17). Note that in (5.10) the term i=3 vanishes as a result of (I.7). It should be noted also that the summation over the particles j in (5.10) contains only those two particles which are involved in the last collision.

The matrix elements in (5.10) contain binary collision operators (2.12) and describe sequences of binary collisions. In this section the collision sequences corresponding to each matrix element will be represented by diagrams, using the notation developed in section III, the only difference being that we don't find it necessary to specify whether the first and last collisions are interacting or non-interacting. In addition the expressions for the matrix elements, which still contain δ-functions through (2.12), are reduced to fourteen dimensional integrals over regions of phase space, where the corresponding collision sequence is geometrically possible. Furthermore, we specify the integrands completely in terms of the integrating variables. Since the reduction of the matrix elements is rather involved, we give the details for two specific examples in a separate appendix B, and simply list the results here.

We consider first the single overlap term μ=2, which can be written as a sum of three terms according to (4.17) and (5.10)

$$[\psi,\chi]_2^{(3)} = [\psi,\chi]_{SS}^{(3)}+[\psi,\chi]_{SN}^{(3)}+[\psi,\chi]_{NS}^{(3)} \quad , \qquad (5.12)$$

where

$$[\psi,\chi]^{(3)}_{SS} = -\int d\vec{v}_1 dx_2 dx_3 \Phi(123)\psi(\vec{v}_1,\vec{v}_2)*\overline{T}_{12}f_{23}G_0 f_{23}T_{13}\chi(\vec{v}_1,\vec{v}_3) \quad , \tag{5.13a}$$

$$[\psi,\chi]^{(3)}_{SN} = -\int d\vec{v}_1 dx_2 dx_3 \Phi(123)\psi(\vec{v}_1,\vec{v}_2)*\overline{T}_{12}f_{23}G_0\overline{T}^n_{23}G_0 T_{13}\chi(\vec{v}_1,\vec{v}_3), \tag{5.13b}$$

$$[\psi,\chi]^{(3)}_{NS} = -\int d\vec{v}_1 dx_2 dx_3 \Phi(123)\psi(\vec{v}_1,\vec{v}_2)*\overline{T}_{12}G_0 T^n_{23}G_0 f_{23}T_{13}\chi(\vec{v}_1,\vec{v}_3), \tag{5.13c}$$

and where we have introduced the shorthand notation

$$\begin{aligned}\psi(\vec{v}_i,\vec{v}_j) &= \psi(\vec{v}_i)+\psi(\vec{v}_j) \quad , \\ \chi(\vec{v}_i,\vec{v}_j) &= \chi(\vec{v}_i)+\chi(\vec{v}_j) \quad .\end{aligned} \tag{5.14}$$

The terms in (5.13) are represented by the diagrams in Fig. 7. In order to express the matrix elements in a compact form we define

$$\Delta_{\sigma_{ij}}\psi(\vec{v}_i,\vec{v}_j) = \psi(\vec{v}_i*,\vec{v}_j*)-\psi(\vec{v}_i,\vec{v}_j) \quad , \tag{5.15}$$

where the velocities $\vec{v}_i*$ and $\vec{v}_j*$ are functions of $\hat{\sigma}_{ij}$, $\vec{v}_i$ and $\vec{v}_j$ as given in (2.13). Using the results of appendix B we find for the SS-collision sequence

$$[\psi,\chi]^{(3)}_{SS} = -\int_{(SS)} d\Omega\Phi(123)\Delta_{\sigma_{12}}\psi(\vec{v}_1,\vec{v}_2)*\Delta_{\sigma_{13}}\chi(\vec{v}_1,\vec{v}_3) \quad , \tag{5.16}$$

where the volume element is

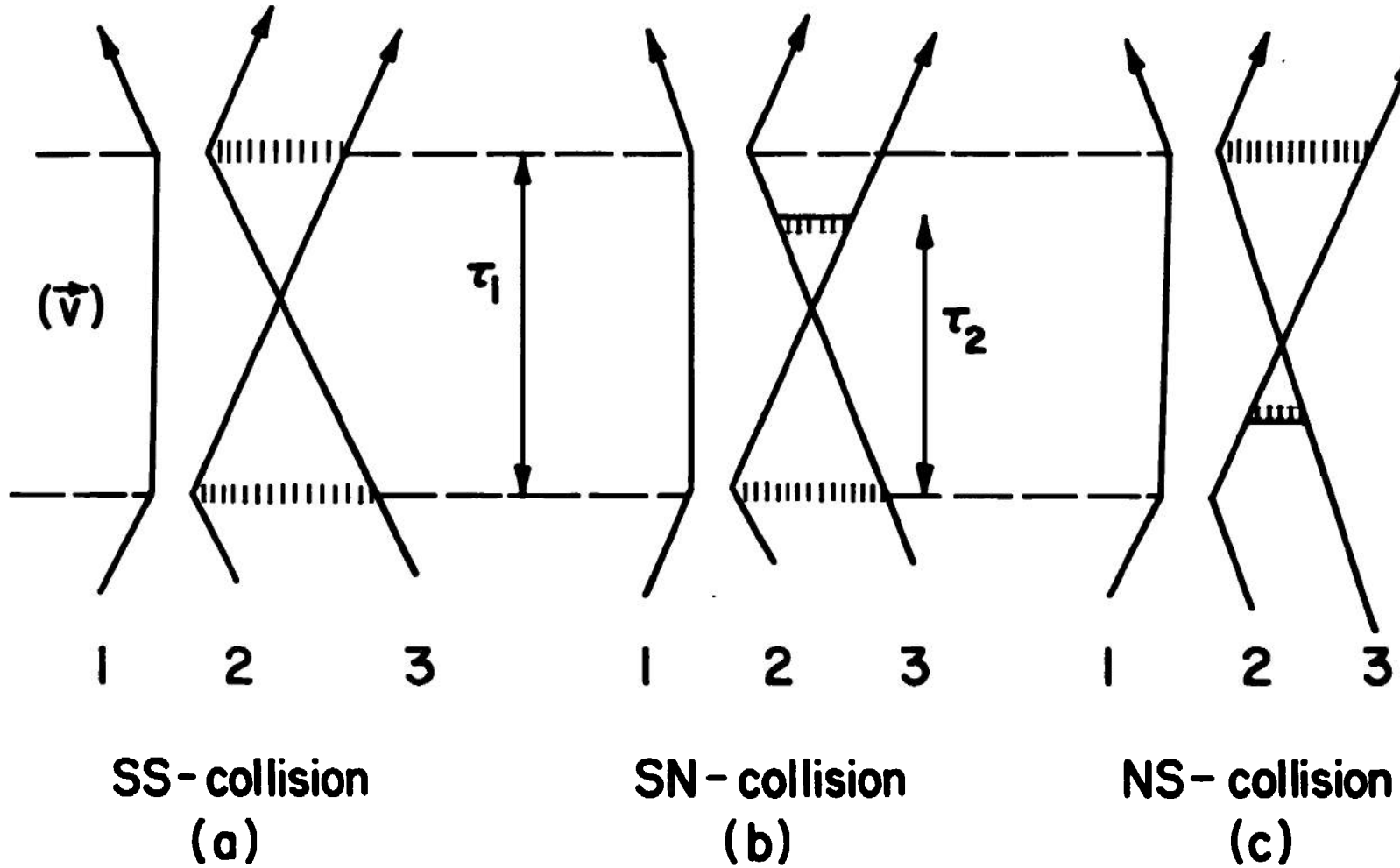

Fig. 7. Diagrams for $[\psi,\chi]_2^{(3)}$.

$$d\Omega = \sigma^2 |\vec{v}_{12}\cdot\hat{\sigma}_{12}| d\hat{\sigma}_{12} d\vec{r}_{13} d\vec{v}_1 d\vec{v}_2 d\vec{v}_3 \ . \tag{5.17}$$

The conditions determining the (SS)-integration region are given by the diagram in Fig. 7a, and read explicitly

$$\vec{v}_{12}\cdot\hat{\sigma}_{12} > 0 \quad ; \quad r_{23} < \sigma \quad ; \tag{5.18a}$$

$$(\vec{r}_{13}\times\vec{v}_{13})^2 - (\sigma v_{13})^2 < 0 \ ; \quad \tau_1 > 0 \quad ; \tag{5.18b}$$

$$\tau_1 < \tau_2 \ . \tag{5.18c}$$

The integrating variables represent the positions and velocities just *after* the first collision. That is, $\vec{r}_{12} = \vec{\sigma}_{12}$ and $\vec{r}_{13}$ refer to the relative positions at the time of the first collision at the bottom of the diagram and $(\vec{v}) = \vec{v}_1, \vec{v}_2, \vec{v}_3$ to the velocities *between* the first and the last collision.

The other symbols are defined in terms of the integrating variables as follows

$$\vec{\sigma}_{13} = \vec{r}_{13} + \vec{v}_{13}\tau_1 \quad ; \quad \vec{r}_{23} = \vec{r}_{13} - \vec{\sigma}_{12} \quad ;$$

$$v_{13}\tau_1 = -\vec{r}_{13}\cdot\hat{v}_{13} - \left[\sigma^2 - (\vec{r}_{13}\times\hat{v}_{13})^2\right]^{1/2} \tag{5.19}$$

$$v_{23}\tau_2 = -\vec{r}_{23}\cdot\hat{v}_{23} + \left[\sigma^2 - (\vec{r}_{23}\times\hat{v}_{23})^2\right]^{1/2}$$

Equation (5.18a) requires that the first collision has occurred, and that it is a single overlap collision (i.e. $r_{23}<\sigma$). The conditions (5.18b) require that the second

collision occurs at some τ_1 *after* the first collision. The time τ_2 is the time between the (12)-collision and the separating (23)-collision. Condition (5.18c) requires that particles 1 and 3 collide *before* 2 and 3 separate, i.e. the (13)-collision is also a single overlap collision.

In the original integral (5.13) the integration extends over the entire phase space of the three particles. The δ-function in the T-operator guaranteed that the integrand would vanish for those phase points for which the required collision sequence would not occur. However, in (5.16) we have integrated over these δ-functions, so that the integration must now be restricted explicitly to those phase points for which the required collision sequence will occur.

Next, we consider the (SN)- and (NS)-terms in (5.12), which are represented by the diagrams in Fig. 7b,c. The contributions of the (SN)- and (NS)-diagrams are related through the symmetry property (4.19), which implies

$$[\psi,\chi]^{(3)}_{SN} = [\chi,\psi]^{(3)}_{NS} \quad . \tag{5.20}$$

The expressions for the matrix elements are

$$\begin{aligned}[\psi,\chi]^{(3)}_{SN} + [\psi,\chi]^{(3)}_{NS} &= \\ &= -\int_{(SN)} d\Omega\Phi(123)\left\{\Delta_{\sigma_{12}}\psi(\vec{v}_1,\vec{v}_2)*\Delta_{\sigma_{13}}\chi(\vec{v}_1,\vec{v}_3) + \right. \\ &\qquad \left. +\Delta_{\sigma_{12}}\chi(\vec{v}_1,\vec{v}_2)*\Delta_{\sigma_{13}}\psi(v_1,v_3)\right\}.\end{aligned} \tag{5.21}$$

The volume element $d\Omega$ is given by (5.17) and the conditions for the integration region now refer only to the SN-collision sequence as determined by the diagram in Fig. 7b, or explicitly, by the conditions (5.18a,b) and

$$\tau_1 > \tau_2 \tag{5.22}$$

The diagrams in Fig. 7a,b show clearly that the conditions (5.18a,b) apply to both diagrams, while the condition, τ_1 smaller or larger than τ_2, distinguishes whether particles 1 and 3 will collide before or after particles 2 and 3 separate.

The corresponding matrix elements $[\psi,\chi]_2^{(\tilde{3})}$ for the self diffusion can be obtained from (5.16) and (5.21) by replacing $\psi(\vec{v}_i,\vec{v}_j)$ and $\chi(\vec{v}_i,\vec{v}_j)$ by $\psi(\vec{v}_1)$ and $\chi(\vec{v}_1)$, respectively.

The collision integrals for $\mu=3$ in (5.10) can be expressed as a sum of three terms

$$[\psi,\chi]_3^{(3)} = [\psi,\chi]_R^{(3)}+[\psi,\chi]_C^{(3)}+[\psi,\chi]_H^{(3)} \ , \tag{5.23}$$

where

$$[\psi,\chi]_R^{(3)} = \int d\vec{v}_1 dx_2 dx_3 \Phi(123)\psi(\vec{v}_1,\vec{v}_2)*\bar{T}_{12}G_o T_{13}^i G_o T_{12}\chi(\vec{v}_1,\vec{v}_2), \tag{5.24a}$$

$$[\psi,\chi]_C^{(3)} = \int d\vec{v}_1 dx_2 dx_3 \Phi(123)\psi(\vec{v}_1,\vec{v}_2)*\bar{T}_{12}G_o T_{13}^i G_o T_{32}\chi(\vec{v}_3,\vec{v}_2), \tag{5.24b}$$

$$[\psi,\chi]_H^{(3)} = -\int d\vec{v}_1 dx_2 dx_3 \Phi(123)\psi(\vec{v}_1,\vec{v}_2)* \bar{T}_{12}G_o T_{13}^n G_o \bar{T}_{13}^n G_o T_{32}\chi(\vec{v}_3,\vec{v}_2). \tag{5.24c}$$

The subscripts refer to the recollision, cyclic collision and hypothetical collision sequences as represented by the diagrams in Fig. 8.

After reduction the recollision term becomes

$$[\psi,\chi]_R^{(3)} = \int_{(R)} d\Omega\Phi(123)\Delta_{\sigma_{12}}\psi(\vec{v}_1,\vec{v}_2)*\Delta_{\sigma^*_{12}}\chi(\vec{v}_1',\vec{v}_2') \quad , \tag{5.25}$$

where the volume element is given by

$$d\Omega = \sigma^2|\vec{v}_{12}\cdot\hat{\sigma}_{12}|d\hat{\sigma}_{12}\sigma^2|\vec{v}_{13}\cdot\hat{\sigma}_{13}|d\hat{\sigma}_{13}d\tau d\vec{v}_1 d\vec{v}_2 d\vec{v}_3 \quad . \tag{5.26}$$

The integration region for the recollision is determined by the diagram in Fig. 8a, or, explicitly, by the conditions

$$\vec{v}_{12}\cdot\hat{\sigma}_{12} > 0 \quad ; \quad \vec{v}_{13}\cdot\hat{\sigma}_{13} < 0 \quad ; \quad \tau > 0 \quad ; \tag{5.27a}$$

$$\{\vec{r}_{12}(2)\times\vec{v}'_{12}\}^2-(\sigma v'_{12})^2 < 0 \quad ; \quad \tau_R > 0 \quad , \tag{5.27b}$$

where we have defined

$$\begin{aligned}
&\vec{\sigma}^*_{12} = \vec{r}_{12}(2)+\vec{v}'_{12}\tau_R \quad ; \quad \vec{r}_{12}(2) = \vec{\sigma}_{12}+\vec{v}_{12}\tau \; ; \\
&\vec{v}_1' = \vec{v}_1-(\vec{v}_{13}\cdot\hat{\sigma}_{13})\hat{\sigma}_{13} \quad ; \quad \vec{v}_2' = \vec{v}_2 \; ; \\
&v'_{12}\tau_R = -\vec{r}_{12}(2)\cdot\hat{v}'_{12}-\left[\sigma^2-\{\vec{r}_{12}(2)\times\hat{v}'_{12}\}^2\right]^{1/2} \quad .
\end{aligned} \tag{5.28}$$

Equation (5.27a) states the condition for the first two collisions to occur, where the integrating variable τ is the time between the first and second collision. Equation (5.27b) gives the requirements for the last collision to occur, where τ_R is the time between the second and third

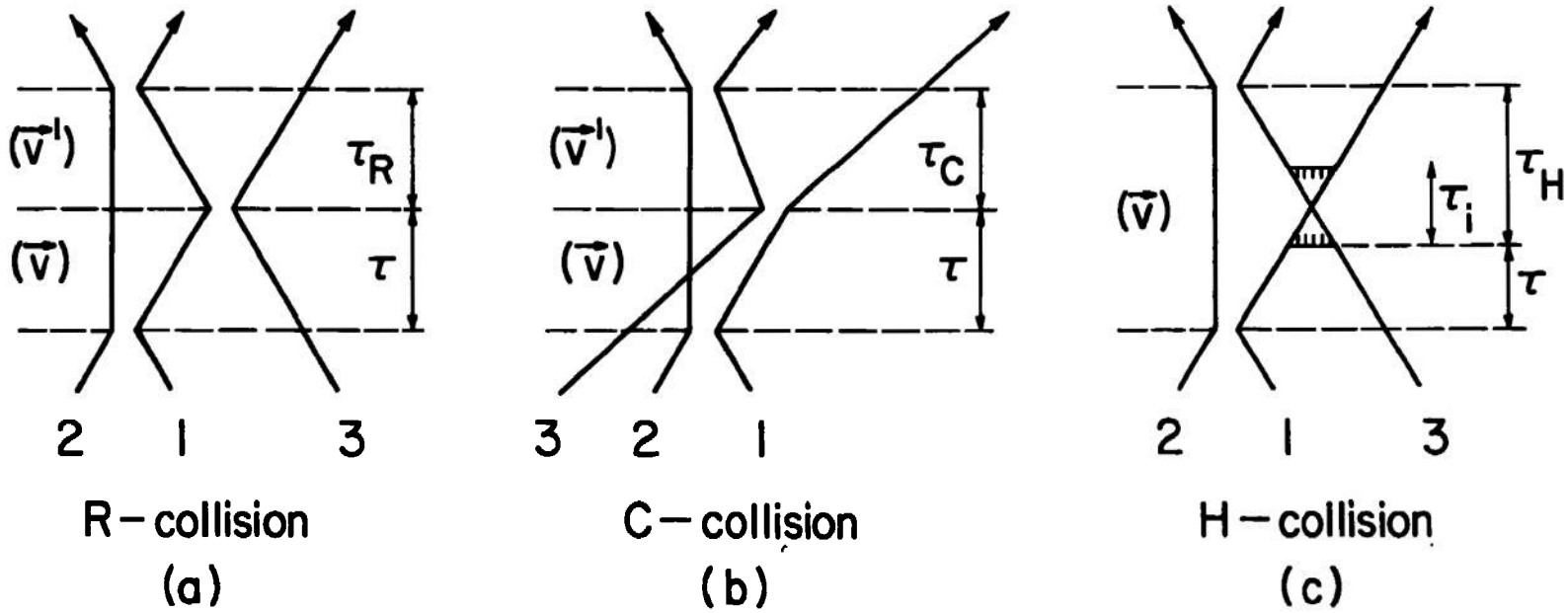

Fig. 8. Diagrams for $[\psi,\chi]_3^{(3)}$.

collision. Primed velocity variables refer to the velocities between the second and third collision, and $\vec{r}_{12}(2)$ is the relative distance between 1 and 2 at the time of the second collision.

We proceed with the cyclic collision term

$$[\psi,\chi]_C^{(3)} = \int_{(C)} d\Omega\Phi(123)\Delta_{\sigma_{12}}\psi(\vec{v}_1,\vec{v}_2)*\Delta_{\sigma_{32}}\chi(\vec{v}_3',\vec{v}_2') \quad , \tag{5.29}$$

where the volume element is again given by (5.26). The integration region for the cyclic collision is determined by the diagram in Fig. 8b, or explicitly by the conditions (5.27a) and

$$\{\vec{r}_{32}(2)\times\vec{v}_{32}'\}^2-(\sigma v_{32}'^{\,2} < 0 \quad ; \quad \tau_C > 0 \quad . \tag{5.30}$$

The quantities used in (5.29) and (5.30) are defined in terms of integrating variables by

$$\begin{aligned}
&\vec{\sigma}_{32} = \vec{r}_{32}(2)+\vec{v}_{32}'\tau_C \quad ; \quad \vec{r}_{32}(2) = \vec{\sigma}_{12}-\vec{\sigma}_{13}+\vec{v}_{12}\tau \quad ; \\
&\vec{v}_3' = \vec{v}_3+(\vec{v}_{13}\cdot\hat{\sigma}_{13})\hat{\sigma}_{13} \; ; \quad \vec{v}_2' = \vec{v}_2 \quad ; \\
&v_{32}'\tau_C = -\vec{r}_{32}(2)\cdot\hat{v}_{32}'-\left[\sigma^2-\{\vec{r}_{32}(2)\times\hat{v}_{32}'\}^2\right]^{1/2} \quad .
\end{aligned} \tag{5.31}$$

The last term in (5.23), represented by the hypothetical collision diagram in Fig. 8c, reads

$$[\psi,\chi]_H^{(3)} = -\int_{(H)} d\Omega\Phi(123)\Delta_{\sigma_{12}}\psi(\vec{v}_1,\vec{v}_2)*\Delta_{\sigma_{32}}\chi(\vec{v}_3,\vec{v}_2) \quad . \tag{5.32}$$

The volume element is again given by (5.26) and the integration

region for the hypothetical collision is determined by the conditions expressed by the diagram in Fig. 8c, or explicitly by (5.27a) and

$$\{\vec{r}_{32}(2)\times\vec{v}_{32}\}^2-(\sigma v_{32})^2 < 0 \quad ; \quad \tau_H > 0 \quad ; \tag{5.33a}$$

$$\tau_H > \tau_i \quad . \tag{5.33b}$$

The above quantities, expressed in integrating variables, are

$$\begin{aligned}
&\vec{\sigma}_{32} = \vec{r}_{32}(2)+\vec{v}_{32}\tau_H \quad ; \quad \vec{r}_{32}(2) = \vec{\sigma}_{12}-\vec{\sigma}_{13}+\vec{v}_{12}\tau \quad ; \\
&v_{32}\tau_H = -\vec{r}_{32}(2)\cdot\hat{v}_{32}-\left[\sigma^2-\{\vec{r}_{32}(2)\times\hat{v}_{32}\}^2\right]^{1/2} \quad ; \\
&v_{13}\tau_i = -2\vec{\sigma}_{13}\cdot\hat{v}_{13} \quad .
\end{aligned} \tag{5.34}$$

Note that (5.33b) expresses the condition that the particles 1 and 3 separate before the (23)-collision, where τ_i is the time particle 3 spends inside the action sphere of particle 1. If we would reverse condition (5.33b), i.e. take $\tau_H < \tau_i$, we would recover the diagram in Fig. 7c and its corresponding (NS)-matrix element.

The corresponding contributions for the self diffusion are

$$\begin{aligned}
[\psi,\chi]_R^{(\tilde{3})} &= \int_{(R)} d\Omega\Phi(123)\sum_{i=1}^{2}\Delta_{\sigma_{12}}\psi(\vec{v}_i)*\Delta_{\sigma_{12}^*}\chi(\vec{v}_i') \quad , \\
[\psi,\chi]_C^{(\tilde{3})} &= \int_{(C)} d\Omega\Phi(123)\Delta_{\sigma_{12}}\psi(\vec{v}_2)*\Delta_{\sigma_{32}}\chi(\vec{v}_2') \quad ,
\end{aligned} \tag{5.35}$$

$$[\psi,\chi]_H^{\tilde{(3)}} = -\int_{(H)} d\Omega\Phi(123)\Delta_{\sigma_{12}}\psi(\vec{v}_2)*\Delta_{\sigma_{32}}\chi(\vec{v}_2) \quad .$$

In order to obtain the collision integrals involving four successive collisions we substitute (5.11) for $\mu=4$ into (5.10) and use (4.16). We thus obtain

$$[\psi,\chi]_4^{(3)} = [\psi,\chi]_{RC}^{(3)}+[\psi,\chi]_{CR}^{(3)}+[\psi,\chi]_{RH}^{(3)}+[\psi,\chi]_{HR}^{(3)} \quad , \tag{5.36}$$

where

$$[\psi,\chi]_{RC}^{(3)} = \int d\vec{v}_1 dx_2 dx_3 \Phi(123)\psi(\vec{v}_1,\vec{v}_2)*\bar{T}_{12}G_oT_{13}^iG_oT_{12}^iG_oT_{32}\chi(\vec{v}_3,\vec{v}_2) \quad ,$$

$$[\psi,\chi]_{CR}^{(3)} = \int d\vec{v}_1 dx_2 dx_3 \Phi(123)\psi(\vec{v}_1,\vec{v}_2)*\bar{T}_{12}G_oT_{13}^iG_oT_{32}^iG_oT_{13}\chi(\vec{v}_1,\vec{v}_3) \quad ,$$

$$[\psi,\chi]_{RH}^{(3)} = -\int d\vec{v}_1 dx_2 dx_3 \Phi(123)\psi(\vec{v}_1,\vec{v}_2)* \bar{T}_{12}G_oT_{13}^iG_oT_{12}^nG_o\bar{T}_{12}^nG_oT_{23}\chi(\vec{v}_2,\vec{v}_3), \tag{5.37}$$

$$[\psi,\chi]_{HR}^{(3)} = -\int d\vec{v}_1 dx_2 dx_3 \Phi(123)\psi(\vec{v}_1,\vec{v}_2)* \bar{T}_{12}G_oT_{13}^nG_o\bar{T}_{13}^nG_oT_{32}^iG_oT_{13}\chi(\vec{v}_1,\vec{v}_3) \quad .$$

The corresponding diagrams are given in Fig. 9. The contributions of the CR-diagram and the HR-diagram are related to those of the RC-diagram and RH-diagram through the symmetry property (4.21)

$$\begin{aligned} [\psi,\chi]_{CR}^{(3)} &= [\chi,\psi]_{RC}^{(3)} \quad , \\ [\psi,\chi]_{HR}^{(3)} &= [\chi,\psi]_{RH}^{(3)} \quad . \end{aligned} \tag{5.38}$$

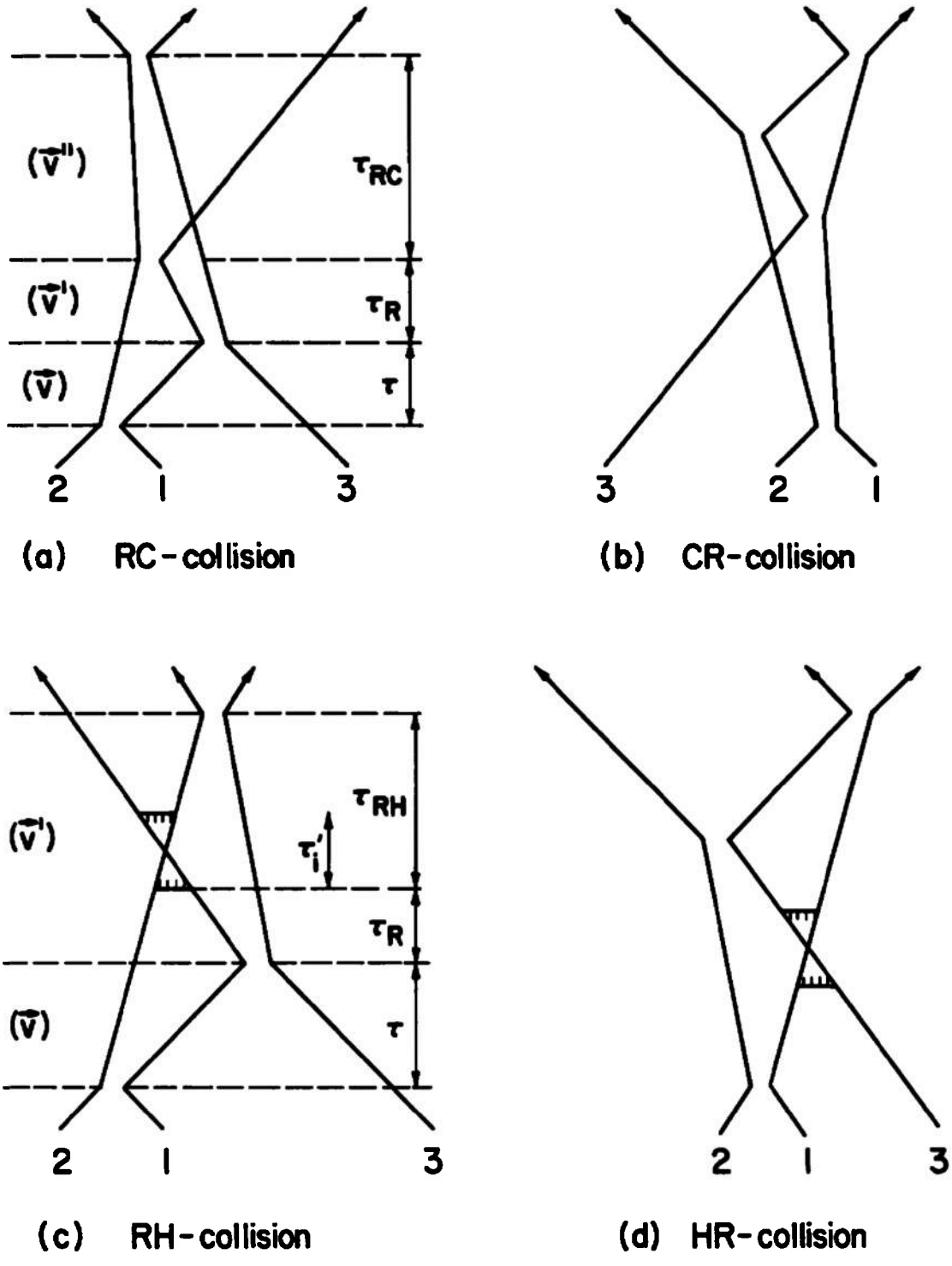

Fig. 9. Diagrams for $[\psi,\chi]_4^{(3)}$.

After integrating out the δ-functions in (5.37) and using (5.38), the matrix element for the RC-collision reduces to

$$[\psi,\chi]^{(3)}_{RC}+[\psi,\chi]^{(3)}_{CR} =$$

$$= \int_{(RC)} d\Omega\Phi(123)\left[\Delta_{\sigma_{12}}\psi(\vec{v}_1,\vec{v}_2)*\Delta_{\sigma_{32}}\chi(\vec{v}''_3,\vec{v}''_2) + \right. \tag{5.39}$$

$$\left. +\Delta_{\sigma_{12}}\chi(\vec{v}_1,\vec{v}_2)*\Delta_{\sigma_{32}}\psi(\vec{v}''_3,\vec{v}''_2)\right] \quad .$$

The volume element dΩ is again given by (5.26). The integration region for the (RC)-collision sequence is determined by the diagram in Fig. 9a, or explicitly by the recollision conditions (5.27) and

$$\{\vec{r}_{32}(3)\times\vec{v}''_{32}\}^2-(\sigma v''_{32})^2 < 0 \quad ; \quad \tau_{RC} > 0 \quad . \tag{5.40}$$

The above quantities can be expressed in terms of integrating variables through (5.28) and in addition

$$\vec{\sigma}_{32} = \vec{r}_{32}(2)+\vec{v}''_{32}\tau_{RC} \quad ; \quad \vec{r}_{32}(3) = \vec{r}_{32}(2)+\vec{v}'_{32}\tau_R$$

$$\vec{r}_{32}(2) = \vec{\sigma}_{12}-\vec{\sigma}_{13}+\vec{v}_{12}\tau \quad ,$$

$$\vec{v}''_2 = \vec{v}'_2+(\vec{v}_{12}\cdot\hat{\sigma}^*_{12})\hat{\sigma}^*_{12} \quad , \quad \vec{v}''_3 = \vec{v}'_3 \quad , \tag{5.41}$$

$$v''_{32}\tau_{RC} = -\vec{r}_{32}(3)\cdot\hat{v}''_{32}-\left[\sigma^2-\{\vec{r}_{32}(3)\times\hat{v}''_{32}\}^2\right]^{1/2}$$

The RH-collision sequence gives the following matrix element

$$[\psi,\chi]^{(3)}_{RH}+[\psi,\chi]^{(3)}_{HR} = -\int_{(RH)} d\Omega\Phi(123)\Big[\Delta_{\sigma_{12}}\psi(\vec{v}_1,\vec{v}_2)*\Delta_{\sigma_{32}}\chi(\vec{v}_3',\vec{v}_2') + \Delta_{\sigma_{12}}\chi(v_1,v_2)*\Delta_{\sigma_{32}}\psi(\vec{v}_3',\vec{v}_2')\Big] \quad , \tag{5.42}$$

with $d\Omega$ as given by (5.26). The integration region for the RH-collision is determined by the diagram in Fig. 9c, or explicitly by the recollision conditions (5.27) and

$$\{\vec{r}_{32}(3)\times\vec{v}_{32}'\}^2-(\sigma v_{32}')^2 < 0 \quad ; \quad \tau_{RH} > 0 \quad . \tag{5.43}$$

In order to define all symbols completely in terms of integrating variables, we need in addition to (5.28) the relations

$$\vec{\sigma}_{32} = \vec{r}_{32}(3)+\vec{v}_{32}'\tau_{RH} \quad ; \quad \vec{r}_{32}(3) = \vec{r}_{32}(2)+\vec{v}_{32}'\tau_R \quad ;$$

$$\vec{r}_{32}(2) = \vec{\sigma}_{12}-\vec{\sigma}_{13}+\vec{v}_{12}\tau \quad ; \tag{5.44}$$

$$v_{32}'\tau_{RH} = -\vec{r}_{32}(3)\cdot\hat{v}_{32}'-\Big[\sigma^2-\{\vec{r}_{32}(3)\times\hat{v}_{32}'\}^2\Big]^{1/2}$$

Note that we have not explicitly imposed the condition $\tau_{RH} > \tau_i'$, where $v_{12}'\tau_i' = -2\vec{\sigma}_{12}^*\cdot\hat{v}_{12}'$, as was done in the comparable case (5.33b). The reason is that contributions from the RH-region where $\tau_{RH} < \tau_i'$ automatically vanish, since we have shown that sequences of four successive collisions cannot contain any overlap collisions (c.f. remark following (4.11)).

The corresponding contributions for the self diffusion are obtained from (5.39) and (5.42) by replacing $\psi(\vec{v}_i,\vec{v}_j)$

and $\chi(\vec{v}_i,\vec{v}_j)$ by $\psi(\vec{v}_2)$ and $\chi(\vec{v}_2)$ respectively.

We remark that the recollisions, cyclic collisions and hypothetical collisions, defined by the diagrams of Fig. 8 have a close resemblance to, but are nevertheless different from, similarly named collision sequences introduced in earlier papers [3,8]. In the present report we have separated the statistical and dynamical correlations, so that the C- and H- collisions in Fig. 8b and 8c do not contain any overlap collisions, in contrast to the collision sequences derived originally. Furthermore, in the earlier formulation the diagrams representing collision sequences had to be supplemented with a number of auxiliary conditions [3,8]. Those conditions effectively accounted for the contributions from sequences of four collisions. In the present report we have shown that the latter contributions can be reduced to two collision integrals defined in terms of the diagrams Fig. 9a and 9c.

VI Discussion

We have shown explicitly how the first density corrections to the transport coefficients of a hard sphere gas are determined by a set of three-particle collision integrals. These collision integrals account for the correlations in the position and velocity variables of three molecules. The correlations are of both a statistical and a dynamical nature. The statistical correlations refer to correlations in configuration space irrespective of the velocities of the particles. For a gas of hard spheres they reduce to excluded volume effects and lead to the consideration of overlap collisions. In an overlap collision the center of at least one of the two colliding particles is constrained to lie inside the interaction sphere of the third particle. These statistical correlations are represented mathematically by Mayer functions (and they are the only correlations to be considered in the density dependence of the *equilibrium* properties.) In addition we need to consider dynamical correlations brought about by sequences of successive collisions. These correlations involve both the position and velocity variables and can be represented mathematically by sequences of binary collision operators.

We have made a systematic analysis of the statistical correlations versus the dynamical correlations. This analysis led to a decomposition of the collision integrals

in terms of integrals associated with the dynamics of *one, two, three* and *four* successive binary collisions among three particles. In order to accomplish this, the triple collision operator was represented by a binary collision expansion. The terms in the binary collision expansion were then ordered such that successive terms in the series correspond to a decreasing number of Mayer functions and increasing number of binary collision operators†. The resulting set of collision integrals is summarized in Table III for easy reference.

As the first term $[\psi,\chi]_1^{(3)}$ in this ordering we recover the coefficient predicted by the theory of Enskog. This collision integral involves the dynamics of only *one* collision, while the positions are correlated by the requirement that both colliding particles must overlap with the third particle. This term, therefore, reduces to the familiar binary collision integral associated with the Boltzmann equation, multiplied with the volume common to the action spheres of two colliding particles.

The second term accounts for the effect of dynamical correlations brought about by sequences of *two* successive collisions. In addition, the positions are now correlated by the requirement that only one of the two colliding particles overlaps with the third particle. This term, therefore, accounts for a combination of excluded volume effects and

†Note that the sequence $T_\alpha G_0 \overline{T}_\alpha$ counts as only one collision, since the operators refer to the penetrating and separating part of the same non-interacting collision.

TABLE III

Summary of three-particle collision integrals

μ (number of successive collisions)	contributing collision integrals	equation	diagram
1	$[\psi,\chi]_1^{(3)}$	(5.7)	(Enskog theory)
2	$[\psi,\chi]_{SS}^{(3)}$	(5.16)	Fig. 7a.
	$[\psi,\chi]_{SN}^{(3)}+[\psi,\chi]_{NS}^{(3)}$	(5.21)	Fig. 7b.
3	$[\psi,\chi]_R^{(3)}$	(5.25)	Fig. 8a.
	$[\psi,\chi]_C^{(3)}$	(5.29)	Fig. 8b.
	$[\psi,\chi]_H^{(3)}$	(5.32)	Fig. 8c.
4	$[\psi,\chi]_{RC}^{(3)}+[\psi,\chi]_{CR}^{(3)}$	(5.39)	Fig. 9a.
	$[\psi,\chi]_{RH}^{(3)}+[\psi,\chi]_{HR}^{(3)}$	(5.42)	Fig. 9c.

dynamical effects. The corresponding collision sequences are represented by the diagrams in Fig. 7, to which we have referred as SS-, SN- and NS-collisions. In the SS-collision, represented by Fig. 7a, both collisions are overlap collisions and in the SN- and NS collisions, represented by Fig. 7b and 7c, only one of the two collisions is an overlap collision.

Correlations caused by sequences of *three* successive collisions are accounted for by collision integrals associated with recollisions, cyclic collisions and hypothetical collisions, defined by the diagrams of Fig. 8. These collision sequences do not contain any overlap collisions.

Finally, the effect of correlations due to sequences of *four* successive collisions is determined by collision integrals defined with respect to the diagrams of Figs. 9a and 9c.

We remark that the same three-particle collision integrals were derived earlier in AEDC-TR-71-51 using geometrical considerations [11,22]. That derivation was based on the cluster expansion of the pair distribution function developed by Green and Cohen [23,24]. An expansion of the three-particle collision integrals in terms of the number of successive collisions was then obtained by decomposing and rearranging the triple collision integrals obtained earlier using a surface-integral method [3,25]. However, that derivation requires rather intricate *geometrical* considerations

and we prefer the more direct *algebraic* derivation presented in this report. Moreover, an attempt was made to give a complete self contained presentation, so that the results do not depend on too many previous papers and reports.

An attempt to separate the statistical and dynamical correlations was made recently by Henline and Condiff [9]. As the first term they also recover the Enskog contribution. In order to assess the contribution from single-overlap collisions, they introduce a term called EVD. This abbreviation indicates that the term incorporates both excluded volume and dynamical effects. However, in deriving this EVD term, Henline and Condiff consider only collision sequences in which the particles overlap *initially*. As a result their EVD term does not account for all collision sequences that involve single-overlap collisions. It corresponds to our collision integrals $[\psi,\chi]^{(3)}_{SS}+[\psi,\chi]^{(3)}_{SN}$, but does not include $[\psi,\chi]^{(3)}_{NS}$. The latter term is equal to $[\chi,\psi]^{(3)}_{SN}$ as shown in (5.20); it is considered by Henline and Condiff implicitly in a term called TC1. The NS-collision sequence, represented by Fig. 7c, is obtained from the SN-collision sequences by time reversal, so that the collision integrals $[\psi,\chi]^{(3)}_{SN}$ and $[\psi,\chi]^{(3)}_{NS}$ have the same physical origin. The matrices of collision integrals associated with the EVD and TC1 terms of Henline and Condiff are not symmetric. In this report we have shown how a systematic

analysis leads to a decomposition of the three-particle collision integrals into matrices that are symmetric. The relationship between our collision integrals and those of Henline and Condiff is shown in Table IV. Henline and Condiff did not consider collision integrals accounting for four collisions involving three molecules.

We have analyzed and calculated the various collision integrals, derived in this report, for all three transport coefficients. A detailed account will be presented in a subsequent technical report.

TABLE IV

Comparison with the collision integrals of Henline and Condiff.

Henline and Condiff	This work
EVD	$[\psi,\chi]^{(3)}_{SS}+[\psi,\chi]^{(3)}_{SN}$
TC1	$[\psi,\chi]^{(3)}_{NS}+[\psi,\chi]^{(3)}_{H}$
TC2	$[\psi,\chi]^{(3)}_{C}$
TC3	$[\psi,\chi]^{(3)}_{R}$

Appendix A. Collisional transfer contributions.

In the main text of this report we have demonstrated how the kinetic contributions λ^{KK}, η^{KK} and D, up to terms linear in the density n, could be obtained from a cluster expansion of the time correlation functions (2.1). In this appendix we show how the potential energy contributions $\lambda^{KU} + \lambda^{UK}$ and $\eta^{KU} + \eta^{UK}$ can be calculated with the same technique.

The potential energy contributions (2.8) to the currents J contain derivatives of the intermolecular potential. For hard spheres it is convenient to eliminate these derivatives by writing the current J(t) as the time derivative of a moment M(t) [29]

$$J(t) = \dot{M}(t) \tag{A.1}$$

with

$$\begin{aligned} \vec{M}_\lambda &= \sum_{i=1}^{N} \left\{ \frac{1}{2} mv_i^2 + \frac{1}{2} \sum_{j \neq i}^{N} U(r_{ij}) - h \right\} \vec{r}_i \quad , \\ \vec{M}_\eta &= \sum_{i=1}^{N} \left\{ m\vec{v}_i \vec{r}_i \right\}_s \quad . \end{aligned} \tag{A.2}$$

The term $U(r_{ij})\vec{r}_i$ in (A.2) vanishes for a gas of hard spheres. Relation (A.1) enables us to relate the current to pseudo-streaming operators. First, we note that the correlation function $\langle J(t_1)J(t_2)\rangle$ depends only on the time difference (t_1-t_2), so that

$$\langle J(t_1)J(t_2)\rangle = \langle \dot{M}(t_1)\dot{M}(t_2)\rangle = -\langle M(t_1)\ddot{M}(t_2)\rangle \quad , \tag{A.3}$$

and, secondly, we have in accordance with (2.15a)

$$\ddot{WM}(t) = WL_N^2 M(t) = \bar{L}_N W L_N M(t). \tag{A.4}$$

The correlation function can now be expressed as

$$\langle J(0)J(t)\rangle = -\sum_N \frac{z^N}{N!Z} \int dx^N \prod_{i=1}^N \psi(v_i) M\bar{L}_N W(12\ldots N) e^{tL_N} L_N M. \tag{A.5}$$

By means of (2.10) and (A.1) we can introduce pseudo currents

$$\begin{aligned} L_N M &= J^K + J_+^U \quad , \\ -\bar{L}_N^+ M &= J^K - J_-^U \quad , \end{aligned} \tag{A.6}$$

with the kinetic parts given by (2.7), and the *collisional transfer* parts

$$\begin{aligned} \vec{J}_{+,\lambda}^U &= \frac{1}{4} \sum_{i\neq j}^N \sum T_{ij} \frac{1}{2} m(v_i^2 - v_j^2) \vec{r}_{ij} - \sum_{i=1}^N h^U \vec{v}_i \\ \vec{\vec{J}}_{+,\eta}^U &= \frac{1}{4} \sum_{i\neq j}^N \sum T_{ij} \left\{ m\vec{v}_{ij} \vec{\vec{r}}_{ij} \right\}_s \quad . \end{aligned} \tag{A.7}$$

Expressions for J_-^U can be obtained from (A.7) by replacing T_{ij} by $\mathcal{T} T_{ij} \mathcal{T}^{-1}$ from table (I.8).

Again we can separate the time correlation functions in KK-, KU-, UK- and UU-parts. The KU- and UK-parts are equal, as can be verified with the help of the relations in Table I. In the present theory the UU-part of the time

correlation function can be neglected, since it contributes only in $O(n^2)$ to the transport coefficients. Hence, to the relevant order in the density we may write down a new time correlation function for $\lambda=\lambda^{KK}+2\lambda^{KU}$ and Section II applies immediately.

Instead of (2.17) we have expressions for the complete λ and η (to the relevant order in n) which can be obtained from (2.17) by replacing the functions Ψ by new functions Ψ' satisfying

$$\Psi'(\vec{v},\varepsilon) = \Gamma(\vec{v},\varepsilon)J(\vec{v})+a(\vec{v},\varepsilon) \quad , \tag{A.8}$$

with

$$\begin{aligned} n\,a(\vec{v}_1,\varepsilon) = 2\sum_{\ell=1}^{\infty}\frac{1}{(\ell-1)!}\int dx^{\ell-1}\prod_{i=2}^{\ell}\phi(v_i)\bar{U}(12\ldots\ell)\cdot \\ \cdot\sum_{N=\ell}^{\infty}\frac{z^N}{(N-\ell)!Z}\int dx^{N-\ell}\prod_{j=\ell+1}^{N}\phi(v_j)W(12\ldots N)J^U \quad , \end{aligned} \tag{A.9}$$

where J^U is given by (A.7).

To lowest order in the density only the term (ℓ=1) contributes to $a(\vec{v};\varepsilon)$. It gives for the heat conductivity

$$\begin{aligned} \vec{a}_\lambda(\vec{v}_1,\varepsilon) &= 2G_o\left\{-h^U\vec{v}_1+n\int dx_2\phi(v_2)W(12)T_{12}\,\tfrac{1}{4}m(v_1^2-v_2^2)\vec{r}_{12}\right\} = \\ &= G_o\tfrac{4}{5}\pi\sigma^3 n\vec{J}_\lambda(\vec{v}_1) \quad , \end{aligned} \tag{A.10}$$

and for the viscosity

$$\overset{\ddagger}{a}_\eta(\vec{v}_1,\varepsilon) = 2G_o n \int dx_2 \phi(v_2) W(12) T_{12} \left\{\frac{1}{2}\vec{m v}_{12}\vec{r}_{12}\right\}_s = \tag{A.11}$$

$$= G_o \frac{8}{15}\pi\sigma^3 n \overset{\ddagger}{J}_\eta(\vec{v}_1) .$$

In the derivation of the integrals (A.10) and (A.11) we have used (2.6), (2.7), (2.12), Table (I.1) and $h^U = p^U/n = \frac{2}{3}\pi\sigma^3 nkT + O(n^2)$ where $p = nkT + p^U$ is the hard sphere pressure. In principle, the term (ℓ=2) in (A.9) could also contribute to O(n), but its contribution vanishes due to (I.2).

Next, we substitute (A.10) and (A.11) in (A.8), multiply (A.8) on the left with Γ^{-1}, and obtain integral equations, similar to (2.27) in which $\overset{\ddagger}{J}_\lambda(\vec{v})$ is replaced by $(1+\frac{4}{5}\pi\sigma^3 n)\overset{\ddagger}{J}_\lambda(\vec{v})$ and $\overset{\ddagger}{J}_\eta(\vec{v})$ is replaced by $(1+\frac{8}{15}\pi\sigma^3 n)\overset{\ddagger}{J}_\eta(\vec{v})$. The final results for the transport coefficients are then

$$\lambda = (1+\tfrac{4}{5}\pi\sigma^3 n)\lambda_o + n\lambda_1^{KK} \quad ,$$

$$\eta = (1+\tfrac{8}{15}\pi\sigma^3 n)\eta_o + n\eta_1^{KK} \quad . \tag{A.12}$$

The terms λ_o and η_o are the Boltzmann values for the hard sphere transport coefficients, the terms proportional to $n\lambda_o$ and $n\eta_o$ are the collisional transfer contributions, and are identical to those obtained from Enskog's theory. The terms $n\lambda_1^{KK}$ and $n\eta_1^{KK}$ are the contributions from triple collisions, calculated in the main text.

Appendix B. Reduction of triple collision integrals.

In this appendix we give the details of the reduction of the triple collision integrals to the explicit forms listed in Section V. As prototypes of this reduction we treat two examples, namely the matrix elements corresponding to the SS-collision and to the recollision.

We start with the matrix element (5.13a), which can be written as

$$[\psi,\chi]^{(3)}_{SS} = -\int d\vec{v}_1 dx_2 dx_3 \Phi(123)\left\{\bar{T}^{\dagger}_{12}\psi(\vec{v}_1,\vec{v}_2)\right\}^{*} \qquad (B.1)$$
$$f_{23}G_o f_{23}T_{13}\chi(\vec{v}_1,\vec{v}_3) \quad ,$$

where we have taken the hermitian adjoint of the $\bar{T}$-operator and used the fact that $\bar{T}^{\dagger}$ commutes with $\Phi(123)$ due to (I.7). According to (2.12), (I.8) and (5.15) one can write.

$$\bar{T}^{\dagger}_{12}\psi(\vec{v}_1,\vec{v}_2) = \sigma^2\int d\hat{\sigma}_{12}|\vec{v}_{12}\cdot\hat{\sigma}_{12}|\Delta_{\sigma_{12}}\psi(\vec{v}_1,\vec{v}_2)\delta(\vec{r}_{12}-\vec{\sigma}_{12}) \quad ,$$
$$\vec{v}_{12}\cdot\hat{\sigma}_{12} > 0 \qquad (B.2)$$
$$\bar{T}_{13}\chi(\vec{v}_1,\vec{v}_3) = \sigma^2\int d\hat{\sigma}_{13}|\vec{v}_{13}\cdot\hat{\sigma}_{13}|\Delta_{\sigma_{13}}\chi(\vec{v}_1,\vec{v}_3)\delta(\vec{r}_{13}-\vec{\sigma}_{13}) \, .$$
$$\vec{v}_{13}\cdot\hat{\sigma}_{13} < 0$$

We further recall that $G_o = (\varepsilon - L_o)^{-1} = \int_0^{\infty} d\tau e^{-\varepsilon\tau}e^{\tau L_o}$, and that the limit $\varepsilon\to 0$ is taken in (B.1). Inserting the above expressions in (B.1) and using (2.5) we find

$$[\psi,\chi]^{(3)}_{SS} = -\int d\vec{v}_1 d\vec{v}_2 d\vec{v}_3 d\vec{r}_{12} d\vec{r}_{13} \Phi(123)\sigma^2 \int_{\vec{v}_{12}\cdot\hat{\sigma}_{12} > 0} d\hat{\sigma}_{12} |\vec{v}_{12}\cdot\hat{\sigma}_{12}| \cdot$$

$$\cdot \delta(\vec{r}_{12}-\vec{\sigma}_{12}) \Delta_{\sigma_{12}} \psi(\vec{v}_1,\vec{v}_2) * \Theta(\sigma-r_{23}) \int_0^\infty d\tau \Theta(\sigma-|\vec{r}_{23}+\vec{v}_{23}\tau|) \cdot$$

$$\cdot \sigma^2 \int_{\vec{v}_{13}\cdot\hat{\sigma}_{13} < 0} d\hat{\sigma}_{13} |\vec{v}_{13}\cdot\hat{\sigma}_{13}| \delta(\vec{r}_{13}+\vec{v}_{13}\tau-\hat{\sigma}_{13}) \Delta_{\sigma_{13}} \chi(\vec{v}_1,\vec{v}_3) \cdot \tag{B.3}$$

In obtaining (B.3), we use the fact that, for any function $F(\vec{r}_{ij},\vec{v}_{ij})$,

$$e^{\tau L} \circ f(\vec{r}_{ij},\vec{v}_{ij}) = f(\vec{r}_{ij}+\vec{v}_{ij}\tau,\vec{v}_{ij}) \quad . \tag{B.4}$$

The appearance of δ-functions allows us to carry out some integrations. Using the first δ-functions in (B.3) we integrate over $\vec{r}_{12}$, so that $\vec{r}_{12}$ has to be replaced everywhere by $\vec{\sigma}_{12}$. The second δ-function will be used to carry out the integrations over τ and $\hat{\sigma}_{13}$. In order to do so we use the relation

$$\int_0^\infty d\tau \sigma^2 \int d\hat{\sigma}_{ij} |\vec{v}_{ij}\cdot\hat{\sigma}_{ij}| \delta^{(3)}(\vec{r}_{ij}+\vec{v}_{ij}\tau-\vec{\sigma}_{ij}) F(\vec{\sigma}_{ij},\tau) =$$

$$\int_0^\infty d\tau \sigma^2 \int_{\vec{v}_{ij}\cdot\hat{\sigma}_{ij} < 0} d\hat{\sigma}_{ij} |\vec{v}_{ij}\cdot\hat{\sigma}_{ij}| \delta^{(1)}(\tau-\tau_\mu) \delta^{(2)}(\vec{r}_{ij}\times\hat{v}_{ij}-\vec{\sigma}_{ij}\times\hat{v}_{ij}) F(\vec{r}_{ij}+\vec{v}_{ij}\tau,\tau)$$

$$= \Theta(\sigma-|\vec{r}_{ij}\times\hat{v}_{ij}|)\Theta(\tau_\mu) F(\vec{\sigma}_{ij},\tau_\mu) \quad , \tag{B.5}$$

where $\vec{\sigma}_{ij}$ and τ_μ on the last line of (B.5) are explicitly given by

$$\vec{\sigma}_{ij} = \vec{r}_{ij} + \vec{v}_{ij}\tau_\mu \quad ,$$
$$v_{ij}\tau_\mu = -\vec{r}_{ij}\cdot\hat{v}_{ij} - \left[\sigma^2 - (\vec{r}_{ij}\times\hat{v}_{ij})^2\right]^{1/2} \quad . \tag{B.6}$$

In the first step in (B.5) the 3-dimensional δ-function is decomposed into a 1-dimensional δ-function for the component of $\vec{r}_{ij}$ parallel to $\vec{v}_{ij}$ and a 2-dimensional δ-function for the components of $\vec{r}_{ij}$ perpendicular to $\vec{v}_{ij}$. In the second step the integrals over the time τ and the solid angle $\hat{\sigma}_{ij}$ are carried out to yield, respectively, the conditions $\Theta(\tau_\mu)$ and $\Theta(\sigma - |\vec{r}_{ij}\times\hat{v}_{ij}|)$; for the $\hat{\sigma}_{ij}$-integration we use the variable transformation $\vec{b} = \vec{\sigma}_{ij}\times\hat{v}_{ij}$ to obtain

$$\sigma^2 \int_{\vec{v}_{ij}\cdot\hat{\sigma}_{ij} < 0} d\hat{\sigma}_{ij} |\vec{v}_{ij}\cdot\hat{\sigma}_{ij}| \delta^{(2)}(\vec{r}_{ij}\times\hat{v}_{ij} - \vec{\sigma}_{ij}\times\hat{v}_{ij}) =$$
$$= \int_{|\vec{b}| < \sigma} d^{(2)}\vec{b}\,\delta^{(2)}(\vec{b} - \vec{r}_{ij}\times\hat{v}_{ij}) = \Theta(\sigma - |\vec{r}_{ij}\times\hat{v}_{ij}|) . \tag{B.7}$$

After carrying out the above integrations we obtain for the relevant matrix element

$$[\psi,\chi]^{(3)}_{SS} = -\int d\vec{v}_1 d\vec{v}_2 d\vec{v}_3 \sigma^2 |\vec{v}_{12}\cdot\hat{\sigma}_{12}| d\hat{\sigma}_{12} d\vec{r}_{13} \quad \cdot$$
$$\cdot\Theta(\vec{v}_{12}\cdot\hat{\sigma}_{12})\Theta(\sigma - r_{23})\Theta(\sigma - |\vec{r}_{23} + \vec{v}_{23}\tau_1|)\Theta(\tau_1)\Theta(\sigma - |\vec{r}_{12}\times\hat{v}_{12}|) .$$
$$\cdot\Phi(123)\Delta_{\sigma_{12}}\psi(\vec{v}_1,\vec{v}_2) * \Delta_{\sigma_{13}}\chi(\vec{v}_1,\vec{v}_3) \quad , \tag{B.8}$$

where

$$\vec{\sigma}_{13} = \vec{r}_{13}+\vec{v}_{13}\tau_1 \quad ; \quad \vec{r}_{23} = \vec{r}_{13}-\vec{\sigma}_{12} \quad ;$$
$$v_{13}\tau_1 = -\vec{r}_{13}\cdot\hat{v}_{13}-\left[\sigma^2-(\vec{r}_{13}\times\hat{v}_{13})^2\right]^{1/2} . \tag{B.9}$$

These results can be put in the form (5.16)-(5.19) of the main text, by realizing that $|\vec{r}_{12}+\vec{v}_{23}\tau_1| < \sigma$ is equivalent with $\tau_1 < \tau_2$, where τ_2 is defined in (5.19). The reduction of the SN -term proceeds along similar lines.

As a second example we treat the recollision term, defined in (5.24a). We start again by taking the hermitian adjoint of $\bar{T}_{12}$ and use relations similar to (B.2). The recollision term can then be written as

$$[\psi,\chi]_R^{(3)} = \int d\vec{v}_1 d\vec{v}_2 d\vec{v}_3 d\vec{r}_{12} d\vec{r}_{13} \Phi(123)\sigma^2 \int_{\vec{v}_{12}\cdot\hat{\sigma}_{12} > 0} d\hat{\sigma}_{12} |\vec{v}_{12}\cdot\hat{\sigma}_{12}| \delta(\vec{r}_{12}-\vec{\sigma}_{12}) \cdot$$
$$\cdot \Delta_{\sigma_{12}} \psi(\vec{v}_1,\vec{v}_2) * \int_0^\infty d\tau\sigma^2 \int_{\vec{v}_{13}\cdot\hat{\sigma}_{13} < 0} d\hat{\sigma}_{13} |\vec{v}_{13}\cdot\hat{\sigma}_{13}| \delta(\vec{r}_{13}+\vec{v}_{13}\tau-\vec{\sigma}_{13}) \cdot$$
$$\cdot \int_0^\infty ds\sigma^2 \int_{\vec{v}'_{12}\cdot\hat{\sigma}^*_{12} < 0} d\hat{\sigma}^*_{12} |\vec{v}'_{12}\cdot\hat{\sigma}^*_{12}| \delta(\vec{r}_{12}+\vec{v}_{12}\tau+\vec{v}'_{12}s-\vec{\sigma}^*_{12}) \Delta_{\sigma^*_{12}} \chi(\vec{v}'_1,\vec{v}'_2) \quad , \tag{B.10}$$

where the prime on the velocity variables represents the action of the operator $R_{\sigma_{13}}$, where $\vec{v}'_{ij} = \vec{v}'_i-\vec{v}'_j$ and

$$\vec{v}'_1 = R_{\sigma_{13}}\vec{v}_1 = \vec{v}_1-(\vec{v}_{13}\cdot\hat{\sigma}_{13})\hat{\sigma}_{13} \quad ,$$
$$\vec{v}'_2 = R_{\sigma_{13}}\vec{v}_2 = \vec{v}_2 \quad . \tag{B.11}$$

The first two δ-functions are used to carry out the integrations over $\vec{r}_{12}$ and $\vec{r}_{13}$. If we introduce the notation

$$\vec{r}_{12}(2) = \vec{r}_{12}+\vec{v}_{12}\tau = \vec{\sigma}_{12}+\vec{v}_{12}\tau \quad , \tag{B.12}$$

the last line in (B.10) has precisely the form of (B.5), so that we can carry out the integrals over s and $\hat{\sigma}^*_{12}$. The result is

$$[\psi,\chi]^{(3)}_R = \int d\vec{v}_1 d\vec{v}_2 d\vec{v}_3 \sigma^2 |\vec{v}_{12}\cdot\hat{\sigma}_{12}| d\hat{\sigma}_{12} \sigma^2 |\vec{v}_{13}\cdot\hat{\sigma}_{13}| d\hat{\sigma}_{13} d\tau .$$

$$\cdot\theta(\vec{v}_{12}\cdot\hat{\sigma}_{12})\theta(\tau)\theta(-\vec{v}_{13}\cdot\hat{\sigma}_{13})\theta(\tau_R)\theta(\sigma-|\vec{r}_{12}(2)\times\hat{v}'_{12}|) \quad . \tag{B.13}$$

$$\cdot\Phi(123)\Delta_{\sigma_{12}}\psi(\vec{v}_1,\vec{v}_2)*\Delta_{\sigma^*_{12}}\psi(\vec{v}'_1,\vec{v}'_2),$$

where all quantities appearing in (B.13) are expressed in terms of integrating variables in (5.28). Equation (B.13) is equivalent with the results (5.25)-(5.28) of the main text.

The remaining collision integrals, corresponding to the C-, H-, RC- and RH-collision can be reduced in a similar way.

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The transport properties of a dilute gas are determined by binary collision integrals. In order to predict the first density corrections to the transport properties, it is necessary to consider collision integrals that account for the effects of collisions among three molecules. In this technical report we derive and formulate such three-particle collision integrals for the coefficients of thermal conductivity, viscosity and self-diffusion of a gas of hard spherical molecules. An evaluation of these three-particle collision integrals will be presented in a subsequent technical report.

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